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A Study on Upgrading of Coal in an Electrothermal Fluidized Bed

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ABSTRACT

A delayed coke produced as a by-product by the Great Canadian Oil Sands contains approximately 5% sulfur and 3% ash. The purpose of this project was to attempt the removal of a substantial amount of the sulfur and ash by a high temperature chlorination technique. If successful, recovery of some of the valuable constituents of the ash was contemplated.

The delayed coke was found to have a relatively small surface area and an almost negligible macro-pore structure. This condition severely restricted the extent to which chlorine could react with the constituents of the coke since this was determined to be a diffusion-controlled reaction.

It was established that

1. The delayed coke, as received, was non-conductive (electrical).
2. Sulfur removal was a function of temperature and time and appeared to be independent of the use of chlorine. About 30% of the sulfur could be removed in ten minutes of temperatures above 1200°C.
3. Removal of ash constituents was not affected by high temperature pyrolysis.
4. The removal of mineral matter was dependent on the presence of chlorine. However, the process was diffusion controlled. At the higher temperatures, it was found that chlorine molecules are capable of diffusing into the coal to react with the inorganic matter; however, the molecular size of the metal chlorides produced precluded their diffusion out of the coke. Roughly 10% of the ash content could be removed in 10 minutes at 1500°C.
5. Chemical comminution of the delayed coke by liquid ammonia produced a product with a slightly larger surface area which enhanced removal

of ash constituents by treatment with chlorine using ammonia pretreated coke. About 30% of the ash content was removed in about 10 minutes at ∿ 1500°C.

6. The structure of the coke as established by others was confirmed by scanning electron micrographs. It appears that the coke may consist of small (2-30 μm) spherical pieces of high purity graphite held in a matrix of ungraphitized carbon which is thought to contain the major portion of the sulfur and ash constituents. The presence of sulfur inhibits the graphitization process. The fact that graphite is difficult to burn accounts for the high carbon content in the fly ash produced at GCOS. The amorphorus-like carbon structure (containing the spherical graphite) is non-conductive but will become conductive after thermal pyrolysis above ∿ 800°C. This is probably due to removal of some of the sulfur and graphitization of the matrix carbon at temperatures above 800°C. In the absence of sulfur, graphitization normally takes place at much lower temperatures, i.e., above 600°C.

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I. INTRODUCTION

1.1 Origin of Problem

The present world energy situation assures that oil from the Alberta tar sands will continue to be recovered. Currently, Great Canadian Oil Sands Ltd. and Syncrude operate the only tar sands projects. The size of the G.C.O.S. operation can be inferred from the data presented Table 1. The Syncrude plant will be approximately twice the size of the G.C.O.S. plant when it reaches full production (1,2).

Focusing on the G.C.O.S. operation, the bitumen as produced in the extraction plant is not suitable for market and therefore must be upgraded before it can be sold. The first major upgrading step involves the coking of the bitumen. At G.C.O.S. this is accomplished by heating the bitumen to approximately 500°C and introducing it into a coking drum at 274 KPa. This is a standard delayed coking operation in which the bitumen is thermally fractured into numerous lighter hydrocarbons, which pass overhead, and heavy coke which is deposited in the drum. A large proportion of the sulphur and almost all of the metals in the bitumen are deposited along with the coke (2,3,4). A typical coke analysis is presented in Table 2.

Of the delayed coke produced, approximately 20% is not burned by G.C.O.S. as indicated by Table 1. This coke is currently being stockpiled without a feasible market, due partially to its high sulphur content. When the delayed coke is burned by G.C.O.S., the fly ash produced contains approximately 30% carbon by weight (1), but values of 50% or more are not uncommon. The high carbon content of the fly ash is more than is normal for coal-fired boilers and suggests

that the coke is difficult to burn under the conditions present in a conventional coal fired boiler. These facts suggest that the development of a commercial method for upgrading the coke (impurity removal) would be of considerable benefit to G.C.O.S.

Table 1

THE G.C.O.S. OPERATION

Total Solids Handled - 300,000 S. tons per day

Tar Sand Mined - 120,000 S. tons per day

Bitumen Produced - 80,000 BPD

Synthetic Crude Oil - 61,000 BPD

Delayed Coke Produced - 3,100 S. tons per day

Delayed Coke Burned - 2,500 S. tons per day

Sulphur Produced - 360 S. tons per day

Table 2

TYPICAL DELAYED COKE ANALYSIS (1)

Component	Weight %
*Fixed Carbon	79
*Moisture	7
*Volatile Matter	11
*Ash	2.8
Sulphur	6
Oxygen	1
Vanadium PPM	800
Titanium PPM	500
Nickel PPM	270

*Proximate Analysis

Although the Syncrude plant produces coke by a lower-coke-yielding fluid-coking process which is a short-residence-time, high temperature operation when compared to delayed coking (4), any development could be useful to Syncrude, or to future operations in the tar sands. Since the coke contains substantial quantities of vanadium, titanium, and nickel, as specified in Table 2, a coke upgrading method that also provided for the recovery of those important metals would be even more beneficial.

Consequently, a coke upgrading scheme involving the high temperature chlorination of the coke was proposed and is investigated in this study. Chlorination at high temperature was selected with the intent of substantially reducing the sulphur content of the coke and converting the mineral matter to volatile metal chlorides which would permit the recovery of specific chlorides through selective condensation. Chlorination has not been previously attempted on coke derived from bitumen, although a number of studies have been conducted on the high temperature chlorination of other carbonaceous materials (11,12,14).

1.2 High Temperature Chlorination Studies for Impurity Removal

Although no data has been reported on the removal of sulphur, mineral matter, or other inorganic impurities from bitumen-derived delayed coke by high temperature chlorination, there have been other studies which provide some basis for comparison with the present investigation. Earlier studies were primarily concerned with purification of graphite. More recent studies have dealt with the purification of other carbonaceous materials, including anthracite coal and petroleum and metallurgical cokes.

Sermon and Brooks (5,6) reported on a method designed to reduce the impurities in pile graphite. Pile graphite is an artificial graphite produced by firing a mixture of petroleum coke and a binder at temperatures up to 2800°C. Graphite blocks were packed in a granular carbon resistance furnace which was electrically heated. The purification procedure consisted of raising furnace temperature to 800°C in a dry nitrogen atmosphere; introducing dry nitrogen saturated with CCl_4 for 3 1/2 hours while increasing the temperature to about 2000°C; then replacing the CCl_4 with Freon-12, CCl_2F_2, for 6 1/2 hours while raising the temperature to about 2500°C. These gases were introduced into the furnace through tubes located directly beneath the graphite blocks.

Sermon et al. showed a reduction of ash from 600 P.P.M. (0.06%) to less than 10 P.P.M., and a reduction of boron from 0.60 P.P.M to less than 0.10 P.P.M. They also indicated that most of the ash was removed by the formation of volatile chlorides, but boron was

specifically removed as a volatile fluoride (obtained from the decomposition of Freon).

A modification of the above process, called the F-process, was later reported by Juel (7). In his work, CF_4, SF_6, and chlorine were used either alone or in combination with CCl_4 and Freon-12, employing a heating cycle similar to that used by Sermon and Brooks. Juel discovered that any of the three reagents reduced the ash content of this pile graphite to below 5 P.P.M. and the boron content to less than 0.10 P.P.M.

When Juel directly chlorinated a raw petroleum coke at a temperature of 1000°C, the product coke contained about 1% chlorine. Up to 20% chlorine was retained by the coke at lower chlorination temperatures. Juel indicated in his study that diffusion may control the purification by chlorination.

One patent (8) described the chlorination of coal and coke at temperatures from 1000 to 1400°C, although levels of impurity removal were not stated. The patent mentions the problem of chlorine attacking the mineral refractory bricks used to line the vertical shaft furnace and suggested the use of carbon brick linings instead.

A similar patent (9) listed results for the chlorination at 1400°C of a coal containing about 10% ash. The resulting coke contained only 2% ash, with iron and aluminum less then 0.2% each, and titanium at 0.05%. The time of treatment was about 12 hours.

Odening and Bowman (10) reported that chlorine treatment was more effective for the removal of all ash impurity constituents except boron, and that Freon-12 appeared to be a specific reagent for boron removal. Their results strongly suggested that the kinetics of the gas purification process were diffusion-rate limited.

Imperial and Walker (11) investigated the removal of mineral matter from anthracite containing about 8% ash by treatment with gaseous chlorine over the temperature range of 600 to 1400°C. A 42 x 65 mesh fraction (Tyler sieve series) of anthracite was employed in most experiments. Reaction conditions included chlorination times from 4 minutes to 6 hours and chlorine concentrations of 25, 50, 75 and 100% in a nitrogen-chlorine mixture. All experiments were conducted at a total pressure of one atmosphere in a reactor consisting of an inner graphite tube and an outer protective ceramic tube with water-cooled metal caps to seal the ends of the tube. They concluded that chlorine was effective in removing mineral matter from anthracite and that the temperature range of 1000 to 1400°C was most effective for purifying purposes. The removal of mineral matter was characterized as being very rapid initially but showing down considerably after a certain chlorination time because of pore diffusion resistance.

Purities corresponding to 95% removal of the original ash content were achieved by chlorination of minus 200 mech anthracite at 1400°C for 6 hours, although titanium and vanadium were found to be most difficult to remove. A reduction of about 20 to 25% in the sulphur content was reported even though sulphur removal was not regarded as a primary objective of the study. The degree of sulphur removal was attributed to be a function of the heat treatment temperature and not of the chlorine atmosphere.

Starzonski and Brothers (12) reviewed a study for the reduction of sulphur content of coke by chlorination. Metallurgical cokes with both high and low sulphur contents were chlorinated with mixtures of argon and chlorine gases in a vertical shaft furnace at atmospheric pressure. A total sulphur reduction of 30% was reported at 50 kPa Cl_2 and a furnace temperature of 550°C. Above 550°C, marginal additional sulphur removal

was obtained. They concluded that: 1) the fixed organic sulphur species were not affected by chlorine at the temperatures used, 2) the degree of sulphur removal was sensitive to Cl_2 partial pressure and 3) the diffusion of chlorine into the coke decreased appreciably after 1 hour exposure.

1.3 Impurity Content of Delayed Coke

Sulphur is normally present in a number of forms, but for many purposes it is convenient to recognize sulphur as being either organic or inorganic. Organic sulphur remains connected to carbon and other atoms by a variety of chemical bonds generally recognized as organic, and is dispersed in the carbon matrix on a molecular level. Inorganic sulphur is largely in the form of pyrites and sulphates, and is found in aggregates throughout the coke structure.

The main purpose in coking bitumen is the liberation of hydrogen from the carbon matrix both as molecular hydrogen and as volatile hydrocarbons. As the temperature is increased, various organic and inorganic sulphur bonds tend to be broken, and the presence of volatizing hydrogen and hydrocarbons assures that some of the sulphur escapes to the gas phase. Thus, depending on the coking process, the resultant coke will contain different species of sulphur in varying quantities. The G.C.O.S. operation produces delayed coke containing 6 weight percent sulphur, on the average, which represents approximately 28% by weight of the original sulphur present in the bitumen feed (1). For comparison, the Syncrude operation produces fluid coke containing 9 weight percent sulphur, on average, which represents approximately 23% by weight of the original sulphur present in the bitumen feed (4).

In both coking operations, most of the mineral matter present in the feed bitumen is deposited in the coke (1, 2, 4). The resultant mineral matter in the coke is thus composed of a large number of constituents. The exact structural nature of these constituents in the coke is not known but they appear to be dispersed throughout the coke structure.

To effect the removal of the sulphur and mineral impurities from the coke, a thermal method could be employed. The sublimation temperature of carbon is higher than the volatilization temperatures of the inorganic impurities, although a temperature close to 3000°C would be required to cause the mineral impurities to volatilize out of the coke structure (11). Therefore, a thermal approach would be technically and economically difficult to implement. Chemical methods, on the other hand, would employ chemical reagents to transform the mineral impurities into soluble or volatile compounds which would then be removed from the coke. These chemical methods have also proven to be technically or economically unattractive (11).

Based on a study of all the information presented here, high temperature chlorination offers a hope of impurity removal from delayed coke.

Many metallic oxides can be converted to volatile chlorides by heating with chlorine. Oxides for which this reaction is possible can be predicted by the magnitude of the free energy change for the chlorination reaction. Table 3 presents values for the standard free energy change ΔG° at 500° and 1000°C for the chlorination of some of the metallic oxides which are probably present in substantial quantities in the delayed coke (13).

ΔG° for the chlorination of iron and nickel oxides are negative and these oxides can theoretically be converted to chlorides by

treatment with chlorine. The chlorination reactions for SiO_2, Al_2O_3, MgO, and TiO_2 have positive values for ΔG°, and the successful use of these reactions is doubtful. The chlorination of these oxides, however, can be effected by the use of chlorine gas and a reducing agent. Carbon, CO, and sulphur have been used as reducing agents for this purpose (13,14).

As shown in Table 4, by using a reducing agent with chlorine, ΔG° for the chlorination of any of the oxides in Table 3 becomes negative and the chlorination reaction is thus theoretically possible under standard conditions.

Table 3

STANDARD FREE-ENERGY CHANGE FOR THE CHLORINATION OF METALLIC OXIDES

Reaction	ΔG° ($\frac{\text{KCAL}}{\text{g-MOLE } Cl_2}$)	
	500°C	1000°C
$1/2\ SiO_{2(s)} + Cl_{2(g)} = 1/2\ SiCl_{4(g)} + 1/2\ O_{2(g)}$	+24.30	+21.40
$1/3\ Al_2O_{3(s)} + Cl_{2(g)} = 2/3\ AlCl_{3(g)} + 1/2\ O_{2(g)}$	---	+ 9.40
$FeO_{(s)} + Cl_{2(g)} = FeCl_{2(g)} + 1/2\ O_{2(g)}$	- 7.60	- 5.20
$NiO_{(s)} + Cl_{2(g)} = NiCl_{2(g)} + 1/2\ O_{2(g)}$	- 9.20	- 6.40
$MgO_{(s)} + Cl_{2(g)} = MgCl_{2(g)} + 1/2\ O_{2(g)}$	+ 4.00	+ 6.20
$1/2\ TiO_{2(s)} + Cl_{2(g)} = 1/2\ TiCl_{4(g)} + 1/2\ O_{2(g)}$	+19.00	+15.90

Table 4

STANDARD FREE-ENERGY CHANGE FOR THE CHLORINATION OF METALLIC OXIDES IN THE PRESENCE OF A REDUCING AGENT (13)

Reducing Agent	Reaction	ΔG° (Kcal/g-MOLECl_2) 500°C	1000°C
Carbon	$1/2\ SiO_{2(s)}+1/2\ C_{(s)}+Cl_{2(g)}=1/2\ SiCl_{4(g)}+1/2\ CO_{2(g)}$	-22.97	-25.94
	$1/3\ Al_2O_{3(s)}+1/2\ C_{(s)}+Cl_{2(g)}=2/3\ AlCl_{3(g)}+1/2\ CO_{2(g)}$	---	-37.94
	$FeO_{(s)}+1/2\ C_{(s)}+Cl_{2(g)}=FeCl_{2(g)}+1/2\ CO_{2(g)}$	-54.87	-52.54
	$NiO_{(s)}+1/2\ C_{(s)}+Cl_{2(g)}=NiCl_{2(g)}+1/2\ CO_{2(g)}$	-56.47	-53.74
	$MgO_{(s)}+1/2\ C_{(s)}+Cl_{2(g)}=MgCl_{2(g)}+1/2\ CO_{2(g)}$	-43.27	-41.14
	$1/2\ TiO_{2(s)}+1/2\ C_{(s)}+Cl_{2(g)}=1/2\ TiCl_{4(g)}+1/2\ CO_{2(g)}$	-28.27	-31.44
	$1/2\ SiO_{2(s)}+C_{(s)}+Cl_{2(g)}=1/2\ SiO_{4(g)}+CO_{(g)}$	-18.80	-32.27
	$1/3\ Al_2O_{3(s)}+C_{(s)}+Cl_{2(g)}=2/3\ AlCl_{3(g)}+CO_{(g)}$	---	-44.27
	$FeO_{(s)}+C_{(s)}+Cl_{2(g)}=FeCl_{2(g)}+CO_{(g)}$	-50.70	-58.87
	$NiO_{(s)}+C_{(s)}+Cl_{2(g)}=NiCl_{2(g)}+CO_{(g)}$	-52.30	-60.07
	$MgO_{(s)}+C_{(s)}+Cl_{2(g)}=MgCl_{2(g)}+CO_{(g)}$	-39.10	-47.47
	$1/2\ TiO_{2(s)}+C_{(s)}+Cl_{2(g)}=1/2\ TiCl_{4(g)}+CO_{(g)}$	-24.10	-37.77
Carbon Monoxide	$1/2\ SiO_{2(s)}+CO_{(g)}+Cl_{2(g)}=1/2\ SiCl_{4(g)}+CO_{2(g)}$	-27.13	-19.60
	$1/3\ Al_2O_{3(s)}+CO_{(g)}+Cl_{2(g)}=2/3\ AlCl_{3(g)}+CO_{2(g)}$	---	-31.60
	$FeO_{(s)}+CO_{(g)}+Cl_{2(g)}=FeCl_{2(g)}+CO_{2(g)}$	-59.03	-46.20
	$NiO_{(s)}+CO_{(g)}+Cl_{2(g)}=NiCl_{2(g)}+CO_{2(g)}$	-60.63	-47.40
	$MgO_{(s)}+CO_{(g)}+Cl_{2(g)}=MgCl_{2(g)}+CO_{2(g)}$	-47.43	-34.80
	$1/2\ TiO_{2(s)}+CO_{(g)}+Cl_{2(g)}=1/2\ TiCl_{4(g)}+CO_{2(g)}$	-32.43	-25.10

Reducing Agent	Reaction	ΔG° (Kcal/g-MOLE Cl_2) 500°c	1000°C
↑	$1/2\ SiO_{2(s)}+1/2\ S_{(s)}+Cl_{2(g)}=1/2\ SiCl_{4(g)}+1/2\ SO_{2(g)}$	-12.20	-10.80
	$1/3\ Al_2O_{3(s)}+1/2\ S_{(s)}+Cl_{2(g)}=2/3\ AlCl_{3(g)}+1/2\ SO_{2(g)}$	---	-22.80
	$FeO_{(s)}+1/2\ S_{(s)}+Cl_{2(g)}=FeCl_{2(g)}+1/2\ SO_{2(g)}$	-44.10	-37.40
Sulphur	$NiO_{(s)}+1/2\ S_{(s)}+Cl_{2(g)}=NiCl_{2(g)}+1/2\ SO_{2(g)}$	-45.70	-38.60
	$MgO_{(s)}+1/2\ S_{(s)}+Cl_{2(g)}=MgCl_{2(g)}+1/2\ SO_{2(g)}$	-32.50	-26.00
↓	$1/2\ TiO_{2(s)}+1/2\ S_{(s)}+Cl_{2(g)}=1/2\ TiCl_{4(g)}+1/2\ SO_{2(g)}$	-17.50	-16.30

1.4 Objective of Investigation

The primary objective of this investigation was to examine the effectiveness of high temperature chlorination for the removal of sulphur and mineral matter from the delayed coke produced by the G.C.O.S. operation. The ultimate goal is to obtain a better fuel and/or a metallurgical coke from the G.C.O.S. material. In addition, chlorination would possibly allow for the recovery of important minerals from the delayed coke as volatile metal chlorides.

To treat the coke under conditions that would approximate those that could be employed industrially, an electrothermal fluidized-bed reactor was employed. This treatment method provided rapid heating of the coke and could be used on a batch or continuous operating basis as required.

Thus, the technical feasibility of using this method of treatment and the problems connected with processing the coke in this manner were to be studied.

II. PRELIMINARY EVALUATION OF DELAYED COKE

2.1 Chemical Analysis

A 400 kg sample of the delayed coke was obtained from G.C.O.S. Since the delayed coke from which the sample was drawn had been stored outdoors before shipment, the sample contained considerable surface moisture and had to be air-dried before use.

The sample originally consisted of coke pieces smaller than 8 cm in size. It was reduced to less than 1.5 cm by successive passes in a jaw crusher. A smaller representative sample was then removed by means of a sample riffle and separated into different size fractions in a Ro-tap Sieve Shaker. The -80+100 mesh (180 μm to 150 μm) Tyler sieve fraction was saved and stored in sealed bottles without further treatment.

A chemical analysis of the -80+100 mesh fraction sample is shown in Table 5. Based on fluidization studies, it was this mesh fraction which was used in all further experiments.

All treated and untreated coke samples were analyzed for moisture, total carbon, total sulphur, chlorine, and ash content. Total sulphur was determined using a Leco sulphur titrator, model 532, in combination with a Leco indiction furnace, model 521. This analytical method used the combustion iodometric procedure which can be found under A.S.T.M. method E30-47. Chlorine in the treated coke samples interfered with the iodometric titration and thus the chlorine in the combustion gases had to be removed by passing the gases through a trap of antimony metal (5).

Total carbon was determined using a Leco gasometric carbon analyzer, model 572-100, in combination with the Leco induction furnace. This

gasometric analyzer is essentially an Orsat analyzer (16). Once again, chlorine interfered and the chlorine in the combustion gases had to be removed by passing the gases through a trap of antimony metal. Figure 1 shows the set up of the Leco apparatus.

Moisture, chlorine, and ash were determined according to methods outlined in A.S.T.M. Standards on Coal and Coke (17). The volatiles, consisting of nitrogen, hydrogen and oxygen were determined by differences and did not include hydrogen and oxygen present as moisture.

Constituents of the ash from the -80+100 mesh fraction of the delayed coke were determined by employing atomic absorption spectroscopy, according to methods described by Pradham (18). An acid digestion bomb was employed to bring the coke ash into solution, thus permitting the determination of ash constituents by atomic absorption.

An analysis of the delayed coke ash is shown in Table 6. The analysis was limited only to the constituents shown due to the limitation of available equipment. The nickel and vanadium contents of the delayed coke ash, as reported in Table 6, are quite high when compared with their level in other coal ashes. For example, a typical anthracite ash contains 0.05 weight percentange V_2O_5 and trace amounts of NiO (1).

Table 5

ANALYSIS OF DELAYED COKE AFTER DRYING

(-80+100 Mesh Fraction)

Weight % Moisture	0.56
On a dry basis:	
Weight % Total Carbon	83.35
Weight % Total Sulfur	5.12
Weight % Chlorine (Cl)	0.00
Weight % Ash	2.90
Weight % Volatiles	8.63
Weight % Total	100.00

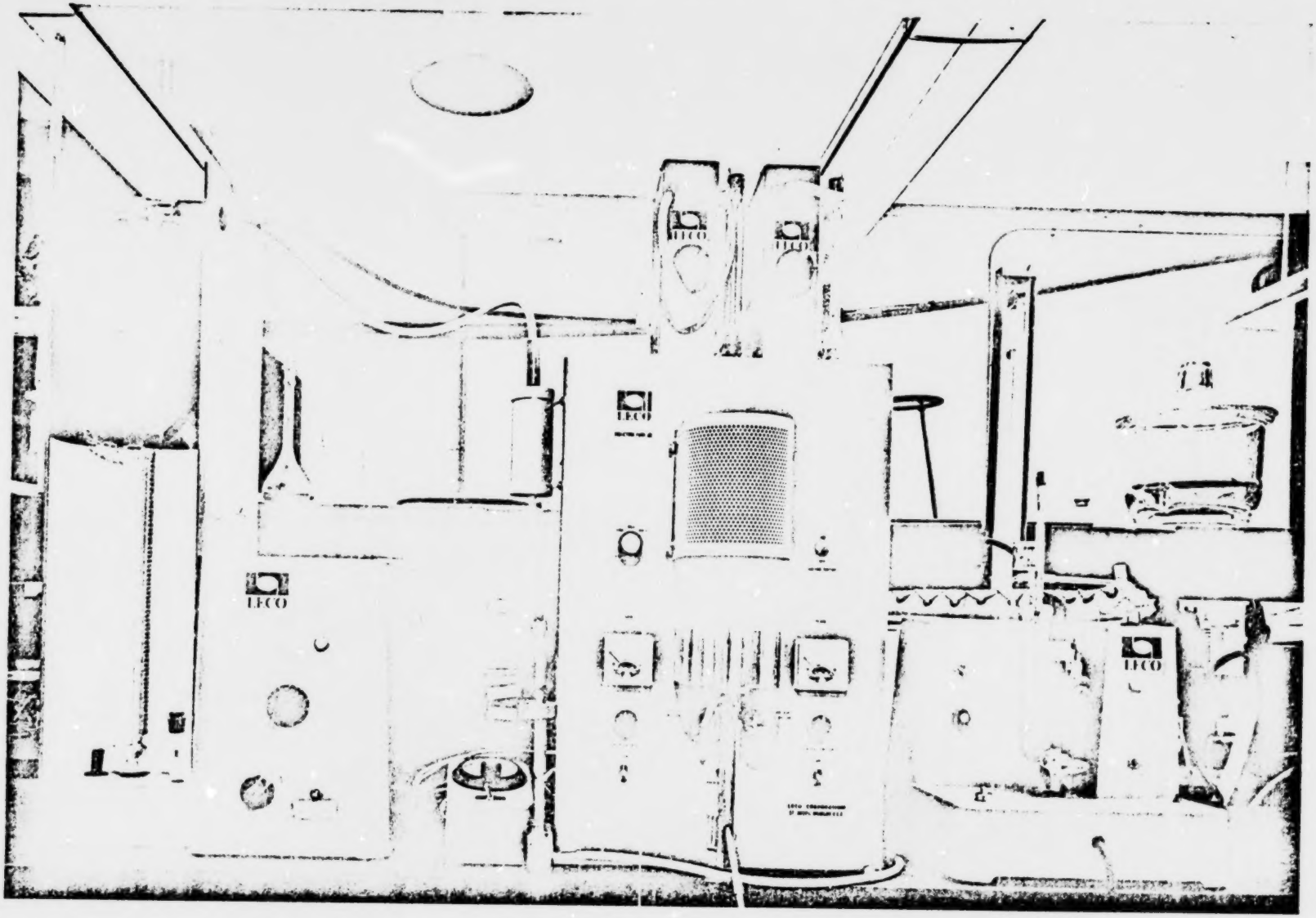
Table 6

ANALYSIS OF DELAYED COKE ASH

Oxide	Weight %
SiO_2	37.40
Al_2O_3	24.90
Fe_2O_3	11.80
V_2O_5	7.41
NiO	1.18
Total	82.69

Figure 1

Apparatus for Carbon and Sulphur Determinations



2.2 Pore Properties

To assess the pore characteristics of the delayed coke, three well known methods were employed: 1) Mercury porosimetry was used to determine the macropore properties, 2) Nitrogen adsorption at liquid nitrogen temperature (-196°C) was used to determine micropore properties, and 3) Carbon dioxide adsorption at 0°C was used to determine ultra-micropore properties.

An Aminco Digital Readout Porosimeter (15,000 psi model) was employed to provide mercury porosimetry data from which cumulative pore volume distribution curves, the total macropore volume and surface area were calculated (20). The delayed coke was found to have a macropore volume of 0.03 cc/g and a surface area of 3.13 m^2/g. These values apply to a pore radium range of 60 Å to 6000°A.

Standard B.E.T. equipment and procedures were employed for both nitrogen and carbon dioxide adsorption on samples of the delayed coke (20). In the case of nitrogen adsorption at -196°C, we used the Brunauer, Emmett and Teller (B.E.T.) adsorption isotherm for the nitrogen adsorption data to obtain a surface area (20), while the pore volume distribution was to be obtained by using the Cranston & Inkly Method which supplies a pore volume and surface area over the pore radius range of 150 Å to 6 Å (21). No nitrogen adsorption was measured. However, since the apparatus used was not capable of measuring adsorption corresponding to less than 1 m^2/g, pore area between 6 and 150 Å must have been less than this value. Nitrogen adsorption on a typical anthracite gives a pore surface area of 1.3 m^2/g (11).

For carbon dioxide adsorption at 0°C, the Dubinin-Radushkevich equation was applied to carbon dioxide adsorption data to obtain a pore volume and surface area over the pore radius range of 2 Å to 15 Å (22). The delayed coke was determined to have a pore volume of 0.06 cc/g and a surface area of 117 m^2/g over this radius range. In comparison, carbon dioxide adsorption on a typical anthracite gives a surface area of 247 m^2/g (11).

Therefore, delayed coke does not present a substantial surface area for chemical reaction with chlorine. Low macropore volumes restrict gaseous diffusion of chlorine into the coke and the counter diffusion of volatiles out of the structure. Furthermore, delayed coke is relatively nonporous on the micropore level. As pointed out previously, the impurity removal efficiency of high temperature chlorination was found by earlier investigators to be diffusion controlled; this observation agrees with the pore area and volume measurements cited above.

2.3 Electrical Resistivity Measurements

Since the operation of the electrothermal fluidized-bed reactor used to treat the coke depends on the electrical resistivity of the coke, it is necessary to know the resistivity of this material.

To conduct these resistivity measurements, a container of 1 cm^2 cross-sectional area with one end closed was constructed from plexiglass. Inside the container, thin copper foil of 1 cm height covered two opposing side walls and extended out the sides of the container where they were attached to the leads of a D.C. ohmmeter.

A coke sample was placed inside the container, without compacting the sample, and the resistance of the material was read from the ohmmeter. The specific resistivity (ρ) in ohm-cm of the sample was calculated from the equation

$$\rho = RA/L$$

where R is the resistance in ohms as measured from the ohmmeter, A is the cross-sectional area of the conduction path through the sample (1 cm^2), and L is the length of the conduction path (1 cm). All measurements of treated and untreated coke were conducted at room temperature.

In this manner, it was discovered that the delayed coke was non-conductive. This fact was cause for concern for the following two reasons. One, most carbonaceous materials with as much carbon as the delayed coke contained were conductive to some extent. Apparently, the structure of the delayed coke must be different from the structure of any comparable carbonaceous material or the coke

is coated with a non-conductive layer. Two, the operation of the fulidized-bed reactor depended on the bed material being partially conductive. This operational problem was overcome as will be described in the next section.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURES

3.1 High Temperature Chlorination

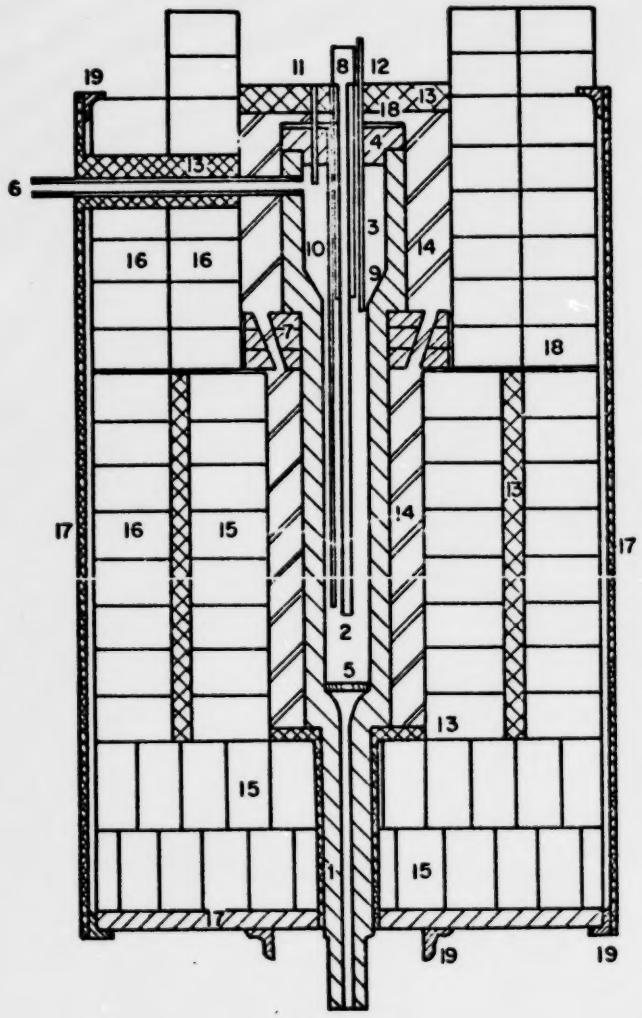
To achieve chlorination of the delayed coke at high temperature, an existing electrothermal fluidized-bed reactor was employed. An internal cross-section of this reactor, showing the details and materials of construction, is presented in Figure 2 (drawn to scale). The distribution plate was removed for our work since the coke was to be bottom fed into the reactor.

The three section reactor body was constructed from one cylindrical piece of high density graphite and thus formed one electrode. The other electrode, which was also constructed of high density graphite, was positioned in the centre of the reactor as shown in the diagram. These electrodes were connected to a Phaser solid state power controller through water cooled power clamps which were attached to the electrodes at the top and bottom of the reactor. The power controller was capable of delivering a maximum power of 120 volts AC at 120 amperes to the reactor electrodes (23). The power controller was connected to the secondary windings of a Hammond 25KVA 60 cycle transformer which provided isolation from the 40 AMP 600 VAC main.

Power delivered to the reactor by the power controller was controlled by means of a Thermac series 6000 Temperature Controller (24). The temperature controller compared the signal from the reactor bed control thermocouple which was either a chromel-alumel or a platinum/6% rhodium-platinum/30% rhodium thermocouple depending on the temperature range being studied. The deviation between the above two signals was transmitted to the power controller as a 0-5 VDC signal. The magnitude of this signal controlled voltage the power controller applied to the reactor electrodes.

Figure 2

The Electrothermal Fluidized-Bed Reactor



0 10 20 cm

LEGEND:

1 GAS PRE-HEATING SECTION
2 FLUIDIZING SECTION
3 DISENGAGING SECTION
4 (GRAPHITE) REACTOR COVER
5 (GRAPHITE) DISTRIBUTOR PLATE
6 (MULLITE) GAS EXIT TUBE
7 (GRAPHITE) SUPPORTING PLATE
8 (GRAPHITE) CENTRAL ELECTRODE
9 TOP GAS INLET TUBE (ALUMINA)
10 BED-THERMOCOUPLE WELL (MULLITE)
11 GAS EXIT-THERMOCOUPLE WELL (MULLITE)
12 ISOLATION TUBE (MULLITE)
13 FIBERFAX ALUMINA FIBER
14 CARBON BLACK
15 REFRACTORY BRICKS
16 FIRECLAY BRICKS
17 TRANSITE SHEET
18 REFRACTORY CEMENT
19 STEEL ANGLES

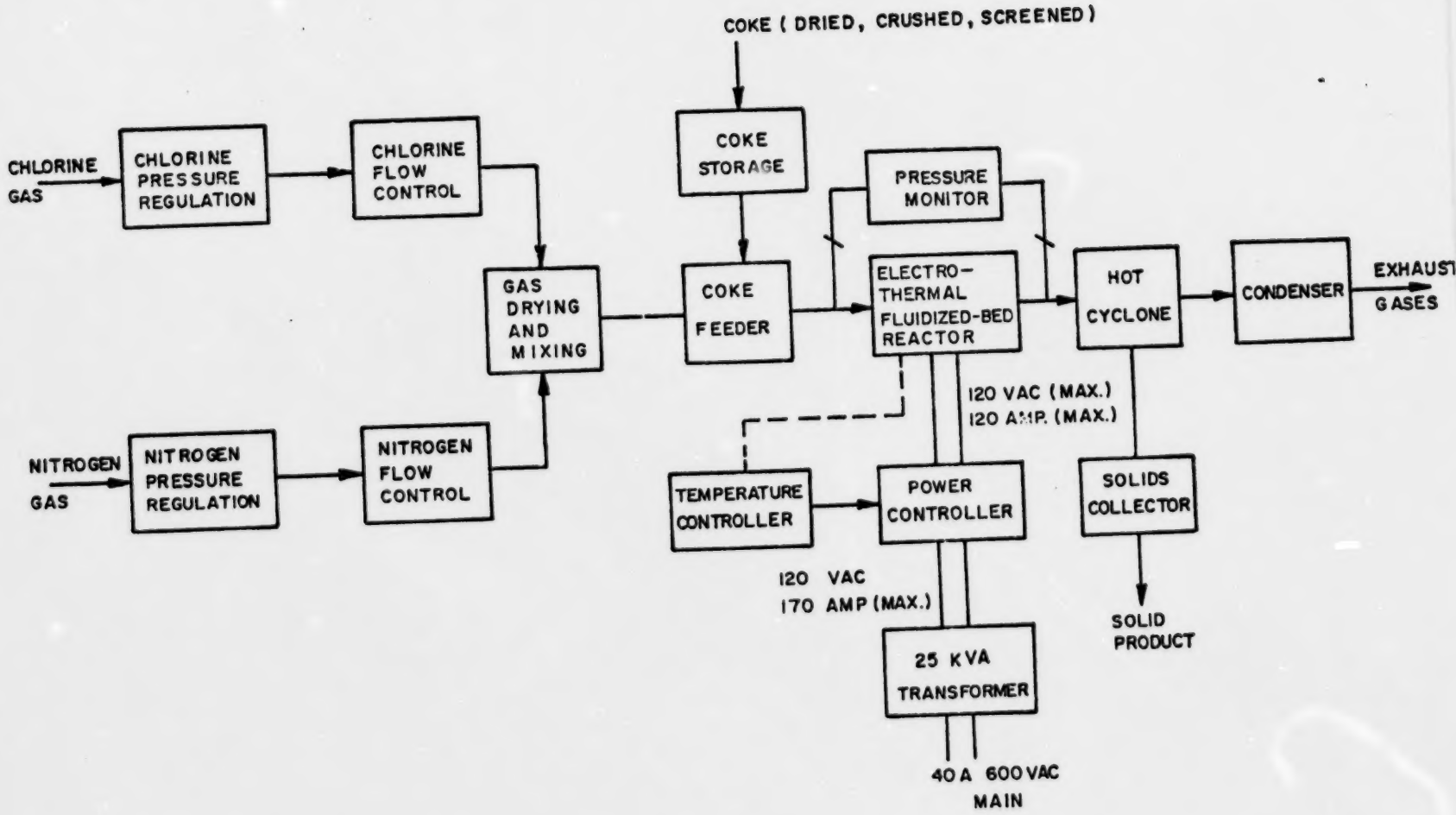
The reactor bed temperature was also monitored by a Honeywell two channel chart recorder through the use either a chromel-alumel or a platinum/6% rhodium-platinum/30% rhodium thermocouple. These thermocouples were positioned at the same depth and in the same bed thermocouple well as the control thermocouple. The temperature in the disengaging section of the reactor was measured by a chromel-alumel thermocouple and recorded on one channel of a Honeywell twelve channel trend recorder.

The electrothermal fluidized-bed reactor operates under the principle whereby the electrical resistance of the bed material, when fluidized by a gas, causes heat to be generated when electrical power is applied to the two reactor electrodes. Thus, the reactor required the presence of a semi-conductive bed between the two electrodes. The degree of gas fluidization of the bed material also influences the resistance between the two electrodes. A fluidization velocity well above the minimum fluidization velocity of the material increases the bed resistance, since the particles forming the bed are separated by a greater distance. These factors controlled the maximum obtainable temperature when full power was applied to the electrodes.

This reactor was chosen because the materials of construction permitted high temperature operation and because the reactor was originally constructed to be resistant to the corrosive attack of chlorine. Resistance heating allows operating temperatures to be obtained quite quickly.

Figure 3 displays the overall high temperature chlorination process flow sheet. Details of the gas and coke feed systems are presented in Figures 4 and 5, respectively.

Figure 3
Block Diagram of High Temperature
Chlorination Apparatus



The high purity nitrogen gas (minimum purity of 99.997%) contained a maximum moisture content of 10 ppm, and a maximum oxygen content of 10 ppm. The liquified chlorine gas had a minimum purity of 99.5%. These gases were usually regulated to a delivery pressure of 308 KPa.

The Scutte and Koerting rotameters on the nitrogen supply line were supplied with calibration curves for nitrogen gas at 21°C and 205 KPa. The Scutte and Koerting rotameter on the chlorine supply line was supplied with a calibration curve for chlorine gas at 21°C and 239 KPa. These calibration curves were corrected for operation at other pressures.

The coke feeder, shown in Figure 5, consited essentially of two presurized lockhoppers to allow for continuous operation. Material to be fed into the reactor was first admitted into the top bin. Both bins were then aspirated and pressurized with nitrogen a number of times to achieve a total nitrogen atmosphere in the two bins. The bins were pressurized with nitrogen gas to the pressure in the gas feed line to the reactor bottom. This was accomplished by the use of the differential pressure controller, which kept the pressure in the bins equal to or slightly above the pressure in the feed bin to the reactor bottom. The material was then dumped into the bottom bin and the two bins were isolated from each other.

When the material was to be fed, a plug valve in the bottom of the lower bin was opened to the desired position. The position of the plug controlled the rate the material was fed into the flowing gas stream below. Once in the gas stream the material was entrained by the gas and carried up into the reaction section of the reactor through the reactor bottom.

Figure 4
Line Drawing of Gas Feed System

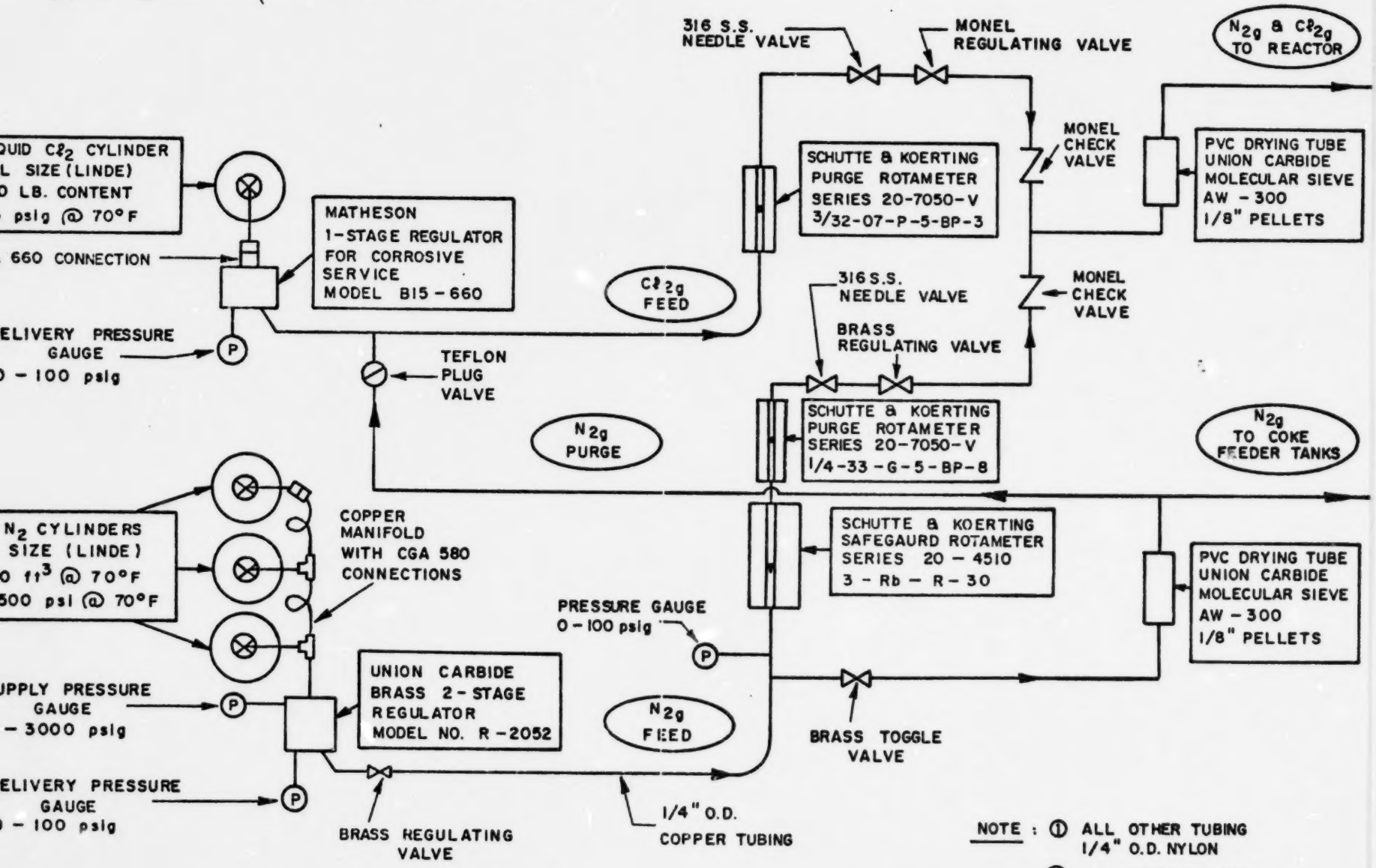
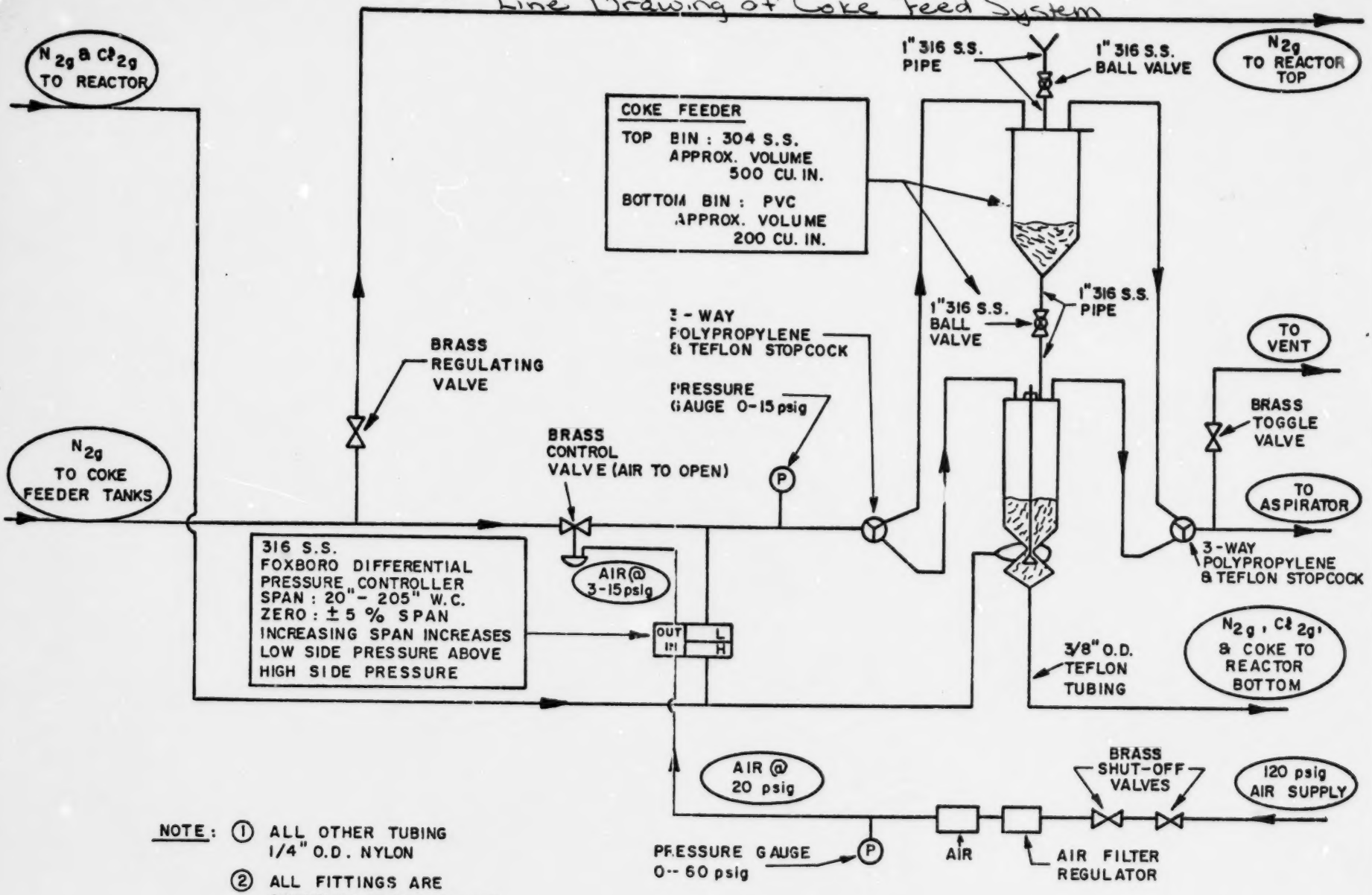


Figure 5.


Line Drawing of Coke Feed System
N_{2g} & Cl_{2g} TO REACTOR
N_{2g} TO COKE FEEDER TANKS
1" 316 S.S. PIPE
1" 316 S.S. BALL VALVE
N_{2g} TO REACTOR TOP
COKE FEEDER
TOP BIN : 304 S.S.
APPROX. VOLUME 500 CU. IN.
BOTTOM BIN : PVC
APPROX. VOLUME 200 CU. IN.
1" 316 S.S. BALL VALVE
1" 316 S.S. PIPE
3 - WAY POLYPROPYLENE & TEFLON STOPCOCK
BRASS REGULATING VALVE
PRESSURE GAUGE 0-15 psig
TO VENT
BRASS TOGGLE VALVE
BRASS CONTROL VALVE (AIR TO OPEN)
TO ASPIRATOR
3-WAY POLYPROPYLENE & TEFLON STOPCOCK
316 S.S. FOXBORO DIFFERENTIAL PRESSURE CONTROLLER SPAN : 20" - 205" W.C. ZERO : ± 5 % SPAN INCREASING SPAN INCREASES LOW SIDE PRESSURE ABOVE HIGH SIDE PRESSURE
AIR @ 3-15 psig
OUT
IN
L
H
3/8" O.D. TEFLON TUBING
N_{2g}, Cl_{2g}, & COKE TO REACTOR BOTTOM
AIR @ 20 psig
BRASS SHUT-OFF VALVES
120 psig AIR SUPPLY
PRESSURE GAUGE 0-60 psig
AIR
AIR FILTER REGULATOR

NOTE: ① ALL OTHER TUBING 1/4" O.D. NYLON

② ALL FITTINGS ARE SWAGELOK TYPE 316 S.S., NYLON, OR BRASS

An overall picture of the system is presented in Figure 6. The hot cyclone, solids collector, condenser, and associated connecting pieces, shown at the left in the pictures, were constructed from quartz and Pyrex. The quartz was attached to the mullite exit tube from the reactor through the use of Sauerisan refractory cement. The Honeywell twelve channel trend recorder, shown in the picture, was used to monitor temperatures at several important locations in the process, through the use of chromel-alumel thermocouples.

Since, as mentioned previously, the delayed coke was non-conductive and the reactor required a semi-conductive bed material for operation, a -20+30 mesh fraction of a conductive petroleum coke was used to bring the reactor up to the required reaction temperature.

The petroleum coke used in these experiments is a very hard, spherical product that withstands the abrasive action in the fluidized bed. This same coke was used in the electrothermal fluid bed studies on the chlorination of zircon and was found to hold up very well under similar high temperature chlorinations.

To begin with, the complete system was purged for half an hour with nitrogen gas. The flow of nitrogen gas was then adjusted to obtain a gas velocity in the reactor reaction section of approximately 1.75 times that required for minimum fluidization of the -20+30 mesh fraction of the metalurgical coke at room temperature. A 1000 cc sample of the -20+30 mesh metalurgical coke was fed into the reactor in the manner discussed previously. Once all the coke was in the reactor, power to the reactor was turned on. As the temperature of the bed material increased, the nitrogen flow rate was reduced to maintain the gas velocity through the bed at approximately 1.75 times the minimum velocity required for

Figure 6
Photograph of High Temperature Chlorination Apparatus

fluidization of the -20+30 mesh matalurgical coke. Table 7 shows the minimum gas flow rates required for fluidization of the -20+30 mesh coke at different temperatures in the reactor reaction section. The reactor was allowed to stabilize for 1 hour once the appropriate reaction temperature was reached.

Table 7

MINIMUM GAS FLOW RATES FOR FLUIDIZATION

(-20+30 mesh petroleum coke)

Temperature (°C)	Minimum Molar Flow Rate (g-moles/min)
20	1.58
100	1.07
200	0.74
300	0.55
400	0.42
500	0.34
600	0.28
700	0.24
800	0.20
900	0.18
1000	0.15
1100	0.14
1200	0.12
1300	0.11
1400	0.10
1500	0.09

The required ratio of chlorine gas to nitrogen gas was then introduced to the reactor, still maintaining the gas velocity through the bed at 1.75 times the minimum at that temperature. Once the reactor was stabilized again, a 60 cc sample (approximately 40 g on the average) of the -80+100 mesh fraction of delayed coke was fed into the reactor. The average feed rate for this material was 10 g/min. After all the delayed coke sample was fed, the reactor was maintained at the reaction temperature for the desired reaction time. During this time, the pressure drop across the bed was consistently on the order of 4.62 KPa, as measured by a mercury manometer. The gas exit from the reactor was essentially at atmospheric pressure.

When the reaction time was completed, the chlorine flow was discontinued and the nitrogen flow increased until the -80+100 mesh material was elutriated from the reactor; the reactor power was then turned off if a subsequent experiment was not to be run. The hot cyclone separated the solid product from the gas stream and deposited the material in the solids collector. Within approximately 6 min. the material was completely removed from the reactor. Once the material cooled down, it was removed from the collector.

The reactor, containing the hot -20+30 mesh metalurgical coke, was then cooled down under a nitrogen flow if a subsequent experiment wasn't to be made. When the reactor temperature dropped to 200° C the nitrogen flow was stopped and the metalurgical coke was dumped out the reactor bottom. Finally, the reactor system was completely purged with nitrogen gas to remove any traces of chlorine gas.

After the reactor experiment, the product material was passed through Tyler sieves to obtain a -80+100 mesh fraction and a -100 mesh fraction. The screening also removed any -20+30 mesh metalurgical coke that was

entrained with the product. The two different fractions of the product material were analyzed for moisture, total carbon, total sulphur, chlorine, and ash contents. The electrical resistivity of the samples were also measured.

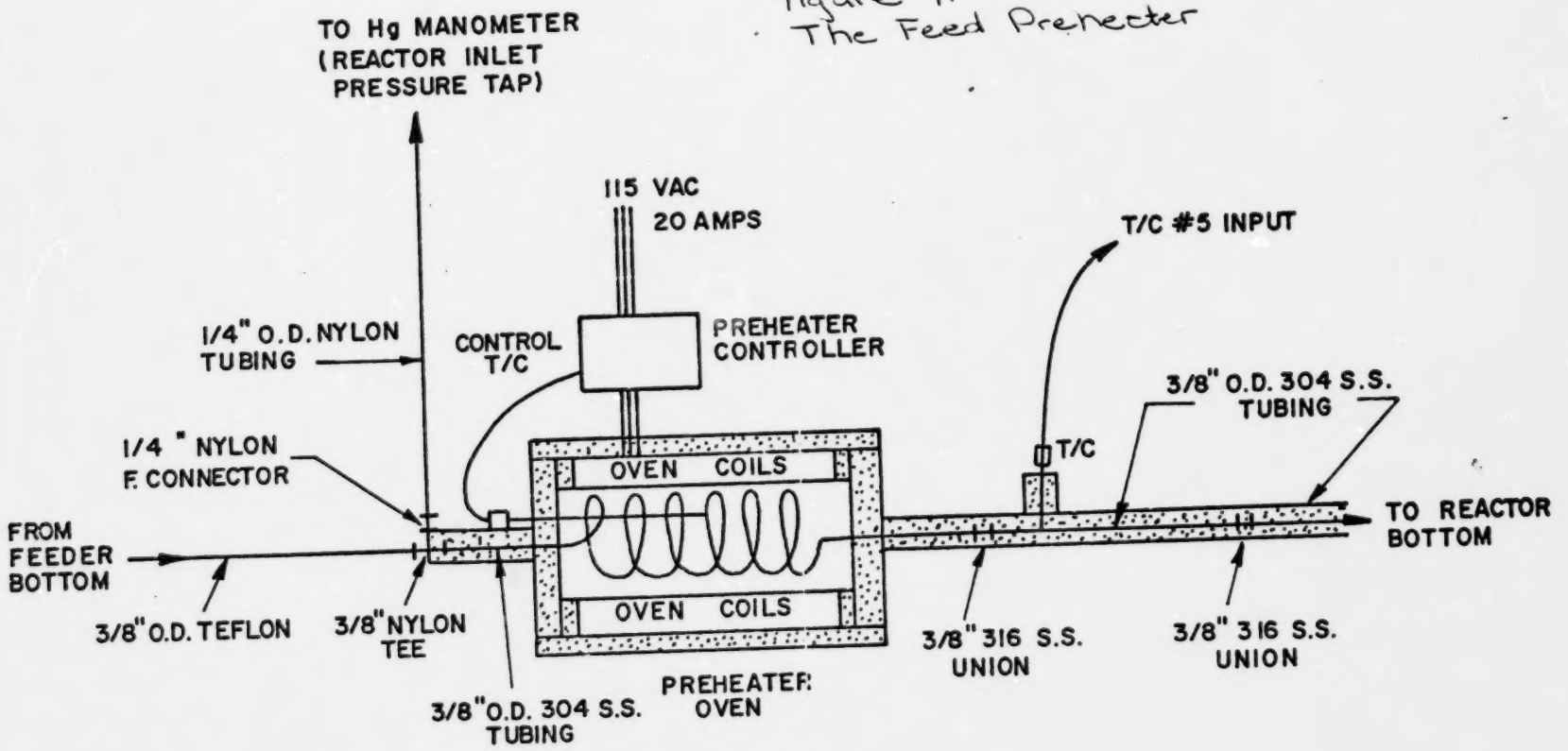
During most of the reactor experiments above 1000°C, considerable difficulty was encountered with the reactor internals. The mullite bed thermocouple well cracked a number of times and had to be replaced. It was decided that the heavy-walled mullite tube was probably cracking from thermal shock when the reacted material was being elutriated from the bed. This protection tube also appeared to be melting on the side closest to the central reactor electrode. The melted appearance of the tube could not be explained, since the bed temperature was always well below the melting point of the mullite. However, pieces of metallurgical coke often became stuck between this tube and the central electrode which could have produced local high temperatures.

This problem was eventually overcome by the addition of the gas preheater, shown in Figure 7, between the coke feeder and the reactor bottom, and the substitution of a quartz bed thermocouple well for the mullite well. The preheater maintained the temperature of the feed gas to the reactor at 170-190°C.

As shown in Figure 8, the quartz protection tube was also partially melted and deformed on the side closest to the central electrode, but only after a number of experimental runs. The quartz tube was smaller in diameter so that the sp cing between it and the central electrode was greater than with the mullite tube, thus precluding coke from being stuck between the thermocouple well and the central electrode.

The experimental investigation was limited to a maximum of approximately 1500°C due to a number of factors. The problems associated with the design

Figure 7.
The Feed Preheater



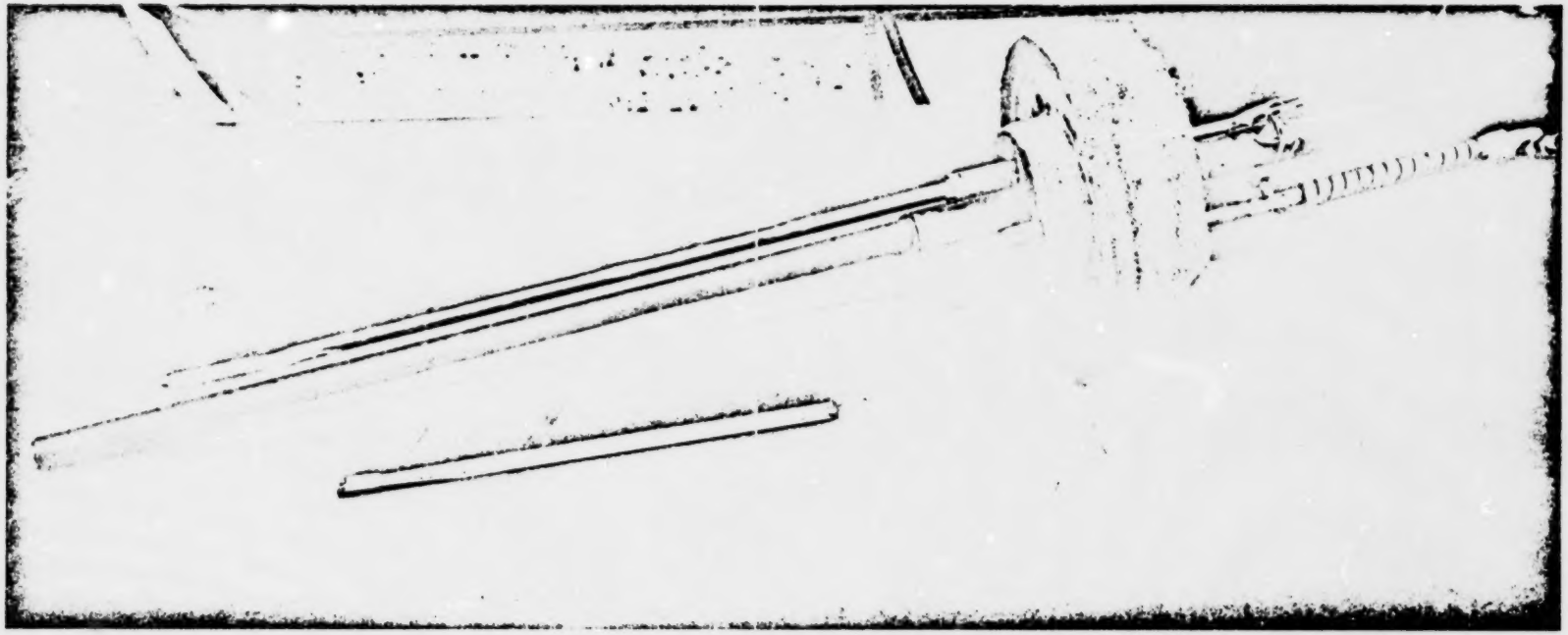
FIBERFRAX INSULATION :

OVEN COILS : 12" LONG
5 1/2" I.D.

PIPE COILS : 8" LONG
5" O.D.

5 T/C WELL : - 2" LENGTH 3/8" O.D. 304 S.S. TUBING WELDED TO OUTSIDE OF 3/8" O.D. 304 S.S. FEED LINE
- 2 1/2" LENGTH PYREX INSERT TUBING CLOSED AT BOTTOM
- # 5 T/C WITH INSULATOR INSIDE PYREX INSERT

Photograph of Reactor Top and Internals



and materials of construction of the previously built electrothermal fluidized-bed reactor, as pointed out above, severely limited the temperature obtainable. Most importantly, the power supply could not raise the temperature much above 1500°C when at full power under the conditions present in the reactor, and even then it was necessary to tightly control the gas velocity in the reactor. Part of this problem relate to the relatively low density of the bed material and the inclination of the bed to de-fluidize when the gas velocity in the bed was well above the calculated minimum fluidization velocity.

3.2 Ammonia Comminution

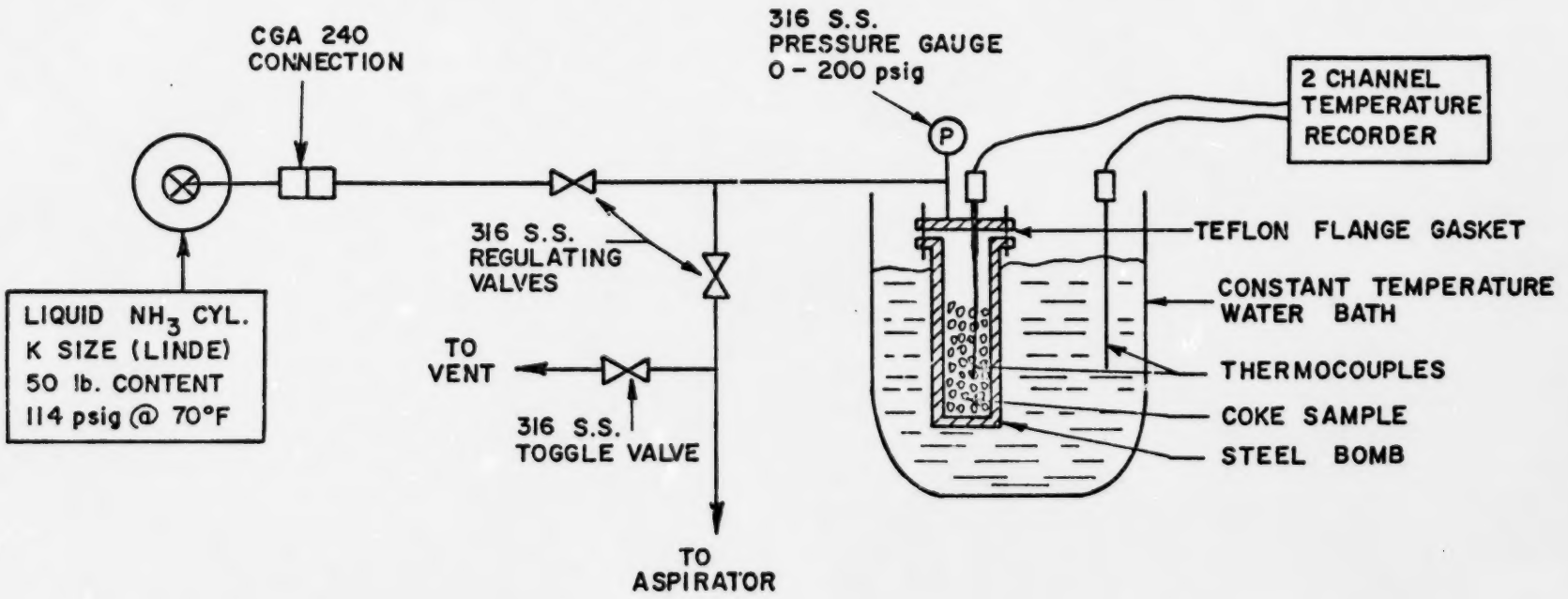
During the course of this investigation, a description of a process for the chemical comminution of coal by ammonia was found (25). It appeared that the method might improve high temperature chlorination by increasing the coke porosity and removing some ash. Chemical comminution is a method for chemically fragmenting coal and is patented by the Syracuse Research Corporation.

The literature gives little information on the mechanism involved in chemical comminution. Keller and Smith (26) proposed that liquid ammonia was imbibed into the coal structure, where the swelling resulted in a strain energy density in a volume of coal which exceeded the fracture stress of the coal. A number of authors (27,28,29), who were associated with the Syracuse Research Corporation, contended that the swelling that occurred was not the classical imbibition effect, but rather, the result of fracturing due to bond interruption along coal/inorganic-constituent interfaces among coal molecules. The chemical agent promoting chemical comminution, namely ammonia, moved throughout this internal fault system by diffusion and/or capillary flow. After selective fragmentation it was rapidly desorbed under ambient conditions without dissolution of the coal matrix nor with any interaction between non-coal constituents and the comminuting agent.

With these concepts in mind, the apparatus shown in Figure 9, was constructed and subsequently used to study the effects of chemical comminution by ammonia on the delayed coke. Delayed coke samples of 2 to 3 cm. size were put into the bomb, shown in the diagram, and aspirated overnight. The bomb was then pressurized with ammonia gas to a pressure of 929 KPa.

Figure 9

Diagram of Ammonia Comminution Apperatus



NOTE : ① ALL TUBING WAS 1/4"O.D. NYLON

② ALL FITTINGS WERE SWAGELOK TYPE 316 S.S.

The bomb surroundings were maintained at different temperatures by means of the water bath shown. After 3 hours time, the bomb was depressurized and the coke sample was removed.

Ammonia exposure did not fragment the delayed coke as was the case for various other coals and cokes under the same conditions (25-27). The delayed coke particles, however, were found to be extremely friable after the treatment. The process also appeared to function better at lower temperatures. The temperature range of 12° to 50°C was studied.

With the idea of using this process as a preliminary method to improve the accessability of chlorine to the internal coke structure during high temperature chlorination, delayed coke was prepared under the above conditions using a bath temperature of 21°C. The treated coke was crushed in a jaw crusher and sieved to remove the -80+100 mesh fraction. This fraction of treated delayed coke was analyzed for moisture, total carbon, total sulphur, chlorine, and ash contents. The effect of the ammonia treatment on the pore properties of the coke was partially examined. A sample of the -80+100 mesh fraction of this treated coke was reacted in the high temperature chlorination apparatus under the previously discussed conditions.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 High Temperature Pyrolysis of Delayed Coke

The purpose of the high temperature pyrolysis experiments was to attempt to separate the effects of temperature from those of chlorination carried out at similar temperatures. Thus the first reactor experiment was conducted using only nitrogen as the fluidizing gas to the electrothermal fluidized-bed reactor. The conditions under which the experiment was conducted are presented in Table 8 along with the analytical results.

The coke product was substantially reduced in size, as indicated in the table, from the feed material of -80+100 mesh size. This size reduction was attributed to degradation of the material by abrasion during feeding and fluidizing the coke. Delayed coke is a very friable material and dusts extensively with any handling. The removal of inorganic matter and sulphur from the coke may also reduce the strength of the original coke and lead to fracture of the grains.

As shown in the table, the size degraded product also became electrically conductive. The finer size range was found to be less resistive (more conductive) than the larger size range. Perhaps the finer size range allows a closer approach of adjacent particles thereby reducing the resistance to current flow.

Results in Table 8, further show that both size ranges of product coke contained less sulphur and volatiles than the original delayed coke contained. On a moisture, chlorine, and volatile free weight basis, the -80+100 and -100 mesh ranges of product coke contained 33.21% and 21.43% less sulphur, respectively, than the original delayed coke.

Table 8

RESULTS OF HIGH TEMPERATURE PYROLYSIS OF DELAYED COKE

Experiment No.		Original Delayed Coke	1	
Reaction Temperature (°C)		--	1490±30	
Reaction Time (Min)		--	5	
Molar Percentage Cl_2 In Fluidizing Gas		--	0.00	
Inlet Temperature of Fluidizing Gas (°C)		--	21	
Weight % of Product Coke Less Than 100 Mesh		--	82.82	
Coke Mesh Range		-80+100	-80+100	-100
Electrical Resistivity (OHM-CM)		∞	3.4×10^3	2.3×10^3
Weight % Moisture		0.56	0.19	0.31
Weight % On a dry basis	Total Carbon	83.35	91.90	86.05
	Total Sulphur	5.12	3.68	4.10
	Chlorine (Cl)	0.00	0.00	0.00
	Ash	2.90	2.93	3.08
	Volatiles (By difference)	8.63	1.49	6.77
	Total	100.00	100.00	100.00

The carbon content, and to some degree the ash content, correspondingly increased to compensate for the decrease in sulphur and volatile content of the product coke. During these experiments, no tarry deposits of material were noticed on the air-cooled condenser; only a very fine coke dust coating was found.

Although the weights of coke fed into and recovered from the reactor for this experiment and succeeding experiments were measured, our results are not reported as impurity removal efficiencies based on product recovery. The reason for this is that relatively small quantities of material were used and some material was lost as extremely fine coke dust throughout the apparatus so that removal efficiencies would not be accurate. Instead, we use component percentage differences between the recovered product coke and the original delayed coke on an equal weight basis to determine the effectiveness of the procedure for impurity removal. Further, to compensate for moisture, chlorine, and volatile content changes during exposure in the fluidized bed, the percentage differences are reported on a moisture, chlorine, and volatile free basis.

As may be seen from Table 8, high temperature pyrolysis alone at approximately 1500°C, removed some sulphur from the delayed coke. The reduction is so limited that pyrolysis without chemical treatment is certainly uneconomical and therefore warrants no further investigation.

Imperial and Walker (1) reported 21% less sulphur in anthracite after thermal treatment in nitrogen at 1400°C. They also observed that the amount of sulphur removed increased with the reaction temperature. Unfortunately, our reactor was limited to a maximum

operating temperature of about 1500°C, further experiments could not be conducted to investigate higher temperatures for delayed coke pyrolysis.

With respect to the removal of mineral matter from the delayed coke, Table 8 shows that high temperature pyrolysis had no effect. This agrees with similar work carried out on coal. In their work with anthracite, Imperial and Walker (11) stated: "It is evident that thermal treatment up to 1200°C in an atmosphere of nitrogen has a negligible or no effect on the removal of mineral matter. Some mineral matter is removed as a result of thermal treatment at 1400°C, but the amount is not sufficient to be of interest".

An explanation for the increase in conductivity is difficult to produce because the structure of delayed coke and its homogeneity are simply not known. It is known that sulphur plays a crosslinking role in tars and pitches and further that on carbonization of those materials, it interferes with the ordering of graphite lamellae associated with graphite. Graphitization will normally begin to take place at temperatures in excess of 600°C, but in the presence of organic sulphur and other volatiles (H_2,O_2) considerably higher temperatures are required. Graphite is, of course, highly conductive. Amorphous carbon conducts poorly. This interpretation is consistent with the simultaneous reduction in sulphur content and the increase in conductivity. Graphitization is almost certainly taking place in the delayed coke at the higher temperature studies in this work.

4.2 High Temperature Chlorination of Delayed Coke

Our main experiments were conducted using a mixture of nitrogen and chlorine as the fluidizing gas to the electrothermal fluidized-bed reactor as explained in the previous section. The conditions under which each experiment was conducted are presented in Table 9 along with the results obtained.

As in the previous preliminary experiment, the coke was substantially reduced in size. No doubt, size reduction resulted from the same processes as in our preliminary experiment, probably abrasion during the feeding and fluidizing steps and perhaps further affected by the removal of both sulphur and inorganic matter from the coke.

It can be seen from the table that the coke product did not become conductive until the reactor temperature reached about 830°C (experiment 4). With succeeding experiments, the electrical resistivity of the product coke decreased to an extent that appears to be directly related to the sulphur content of the product coke and the reaction temperature for that experiment. Figure 10 illustrates these observations. Imperial and Walker (11) also reported a decrease in resistivity with increasing chlorination temperature for anthracite coal. They also showed that for comparable treatment temperatures, the chlorinated anthracite always possessed a lower resistivity than the pyrolyzed anthracite. This result is substantiated by comparing the resistivity values for either experiment No. 8 or 9 in Table 9, with the resistivity values for experiment No. 1, in Table 8 where virtually the same temperatures were employed in all cases. The pertinent figures are shown below:

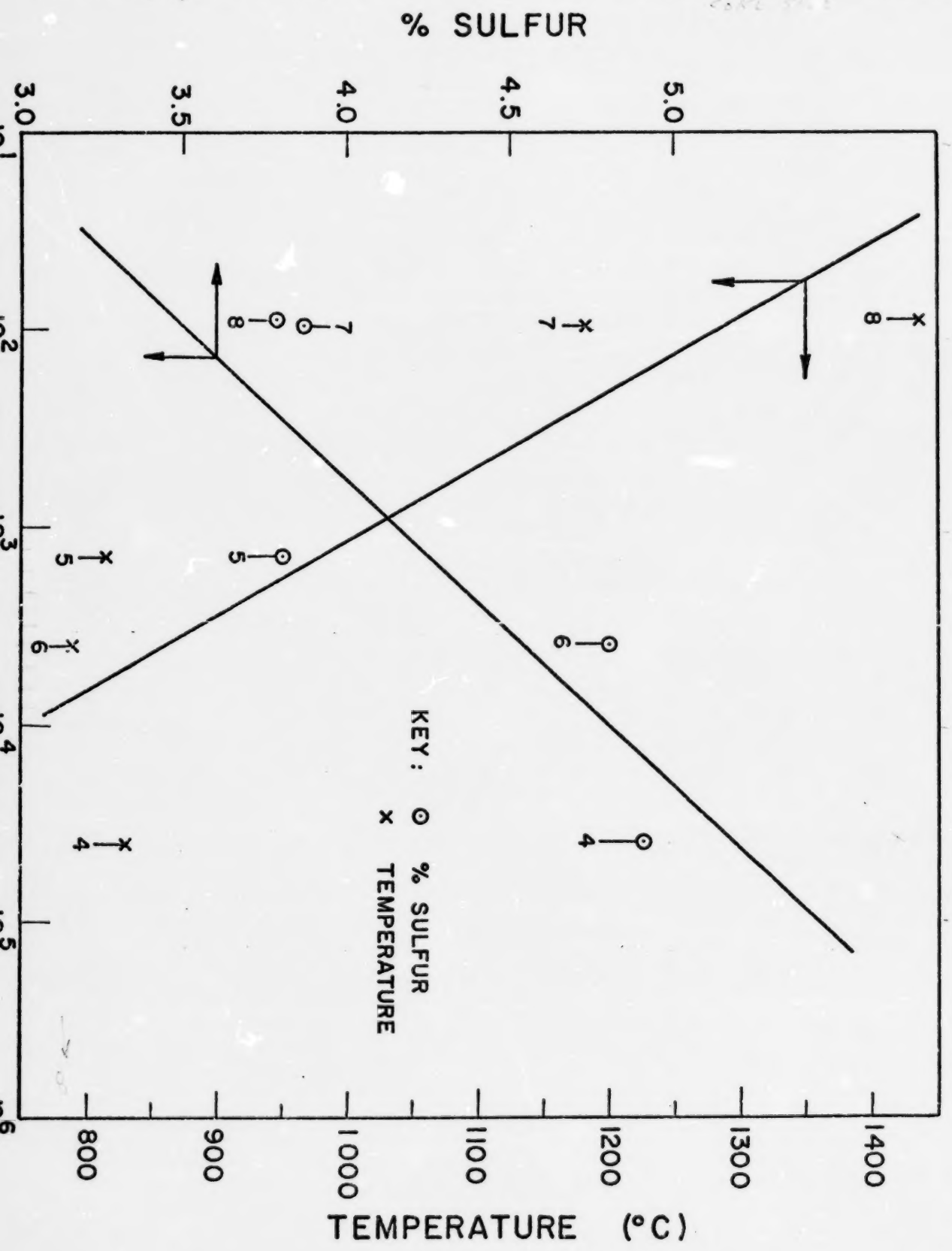
Table 9

RESULTS OF HIGH TEMPERATURE CHLORINATION OF DELAYED COKE

Experiment No.	Orig. Delayed Coke	2	3 *		4	5	6 *		7	8 *		9					
Reaction Temp. (°C)	--	500±51	1. 625±47 2. 600±34		830±25	815±12	1. 790±10 2. 995±43		1183±37	1. 1335±69 2. 1437±33		1498±22					
Reaction Time (MIN).	--	12	1. 15 2. 5		10	10	1. 10 2. 10		10	1. 5 2. 10		60					
Molar Percentage Cl_2 in Fluidizing Gas	--	0.11	1. 0.15 2. 0.00		0.21	> 0.21 < 25.00	1. 25.00 2. 0.00		25.00	1. 2.70 2. 2.70		3.23					
Inlet Temp. of Fluidizing Gas (°C)	--	21	1. 21 2. 21		21	21	1. 21 2. 21		205	1. 180 2. 183		165					
Weight % of Product Coke Less than 100 Mesh	--	61.74	49.15		65.13	78.33	62.94		61.31	83.04		81.49					
Coke Mesh Range	-80 +100	-80 +100	-100	-80 +100	-100	-80 +100	-100	-80 +100	-100	-80 +100	-100	-80 +100	-100	-80 +100	-100	-80 +100	-100
Electrical Resistivity (OHM-CM)	∞	∞	∞	∞	∞	$4.0_4 \times 10^4$	$2.8_4 \times 10^4$	$1.4_3 \times 10^3$	$5.5_2 \times 10^2$	$4.0_3 \times 10^3$	$3.2_3 \times 10^3$	$9.5_1 \times 10^1$	$1.9_2 \times 10^2$	$9.0_1 \times 10^1$	$8.1_1 \times 10^1$	$4.0_2 \times 10^2$	$6.5_2 \times 10^2$
Weight % Moisture	0.56	3.97	5.37	5.11	4.55	0.97	1.19	1.90	1.65	1.93	1.98	1.26	2.07	0.44	0.73	2.72	2.02
Weight % on a dry basis: Total Carbon	83.35	76.50	77.84	84.85	80.36	91.78	90.20	72.91	73.58	83.34	82.77	86.54	84.83	88.29	84.83	78.25	83.63
Total Sulphur	5.12	4.98	4.70	4.76	4.85	4.90	4.72	3.80	3.93	4.81	4.48	3.87	3.58	3.78	3.76	2.80	2.71
Chlorine (Cl)	0.00	0.96	0.70	0.44	0.70	0.09	0.09	7.36	6.81	0.76	1.49	6.92	7.20	2.26	2.79	3.87	3.76
Ash	2.90	2.70	2.56	2.64	3.39	3.23	3.52	2.75	2.78	3.27	3.20	2.62	4.39	1.94	2.80	2.79	3.28
Volatiles (by difference)	8.63	14.86	14.20	7.31	10.70	0.00	1.47	13.18	12.90	7.82	8.06	0.00	0.00	3.73	5.82	12.29	6.62
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* The conditions shown besides 1. and 2. represent the conditions present during the first and second parts of the same experiment.

Figure 10.
Trend in the Variability of Electrical Resistivity with Sulphur Content of the Coke and Temperature of Treatment



Exp. No.	1	8	9
Electrical * Resistivity	3.4×10^{3}	0.9×10^{1}	4×10^{2}

* -80+100 mesh fraction

In most cases the finer size range of coke product was less resistive than the coarse size range. As mentioned earlier, this may be explained by geometric onsiderations whereby the finer size range allows a closer approach of adjacent particles or perhaps by arguing that the finer size range contains more newly reacted surface than the coarser size range.

A number of overall trends are evident in Table 9. The most noticeable is the ability of the delayed coke to retain chlorine after high temperature chlorination at all reaction temperatures examined. In some cases (Exp. 5,7,9), the apparent retention is very significant. At high temperature, chlorine will apparently chemisorb on peripheral carbon atoms to form primarily ionic bonds (11). Only a small portion of the retrained chlorine could be due to chlorine absorption into pores, since the delayed coke is not very microporous, as reported previously. Crude calculations of the adsorption cross-section of the coke indicate that approx. 1.5×10^{-3} moles of Cl_2 per gram of coke could be adsorbed on the surface of the coke, assuming a monomolecular layer phenomena; this figure compares with a value of 1×10^{-3} when the coke analysis showed 7% Cl_2 so adsorbed.

Chlorine retention by the coke seemed to increase as the temperature of chlorination increased. Comparing experiment No. 9 with No. 8, a very large increase in chlorination time at comparable reaction

temperatures did not cause a large increase in chlorine retention. However, chlorine retention by the coke at comparable reaction temperatures increases as the molar percentage of chlorine in the fluidizing gas increases, as evidenced by experiments No. 4 and 5. Comparing the results of experiment No. 6 with those of No. 5, an increase in reaction temperature without chlorine above the comparable chlorination temperature, reduced the chlorine retention of the coke.

Table 9 shows a noticeable but erratic increase in the volatile content of the product coke after treatment. Table 8 on the other hand shows a decrease in volatiles after pyrolysis. The original volatile content of the delayed coke consisted primarily of nitrogen, oxygen, and hydrogen, probably absorbed and perhaps some residual decomposable carbon compounds. The increase in the volatile content could only be due to chlorides which were formed and unable to volatilize out of the coke structure and therefore, would add to the total weight of the sample before chemical analysis. Volatile chlorides have larger collision diameter than chlorine and could be trapped thereby. An increase in volatile matter was also observed by Imperial and Walker (11).

A consistent increase in the moisture content of the product coke over that in the original delayed coke was also experienced. The fact that almost all metal chlorides are hygroscopic is perhaps the main reason for the observation. Another plausible explanation is that loosely adsorbed chlorine in the coke pores is detected as moisture by the methods used to determine the moisture content of coke samples.

However, no patterns can be seen in Table 9 between moisture or volatile content or one side and chlorine content on the other.

Essentially no sulphur removal from the delayed coke was experienced until at least 600°C was attained (experiment No. 3). This result could have been anticipated since the delayed coke was formed in a process at a temperature of approximately 500°C (2,3,4). As the chlorination temperature increased, the removal of sulphur increased. A similar result was observed by Imperial and Walker (11). This trend continued until 1180°C (experiment No. 7) after which the difference in sulphur content between the product coke and the original delayed coke remained essentially constant at about 27%, on a moisture, chlorine, and volatile free weight basis. The run at 1500°C (experiment No. 9) was an exception. By increasing the reaction time to 60 minutes, the difference in sulphur content between the product coke and the original delayed coke increased to around 45%, on a moisture, chlorine, and volatile free weight basis. Imperial and Walker (11) reported reductions in sulphur content of about 20-25% for chlorination of anthracite at temperatures between 1000 and 1400°C.

In experiment No. 6 the reaction temperature was increased to approximately 1000°C without chlorine after treatment with chlorine at a temperature of approximatley 800°C. On a moisture, chlorine, and volatile free weight basis, the percentage difference in the sulphur content between the product coke and the original coke was comparable to the values obtained for experiment No. 4 and 5, at a chlorination temperature of approximately 800°C. This observation suggests that the removal of sulphur from the delayed coke depends on chlorine

being present at the reaction temperature. The dependence of sulphur removal on the concentrations of chlorine used must be very small as experiment No. 4 and 5 both at a chlorination temperature of approximately 800°C seems to show. The percentage difference in sulphur between the product coke and the original coke was similar, on a moisture, chlorine, and volatile free weight basis for these runs.

Mineral matter removal from the delayed coke was experienced at temperatures above 1180°C (experiment No. 7). On a moisture, chlorine, and volatile free weight basis, the -80+100 and -100 mesh ranges of product coke at 1330 to 1445°C contained 35.22% and 3.77% less mineral matter, respectively, than the original delayed coke contained. The coke product from experiment No. 9, at a comparable reaction temperature but extended reaction time, actually contained more mineral matter than the original delayed coke contained. This apparently contradictory result was due to the large sulphur loss from the delayed coke. In other words, extending the chlorination time did not increase the amount of mineral matter removed but it did increase sulphur removal causing an apparent increase in ash content on the comparison basis we use. Effectively, a limit in mineral matter removal is reached. Imperial and Walker (11) reported that the rate of mineral matter removal from anthracite essentially stops after 12 minutes of reaction time, at chlorination temperatures above 1000°C.

During experiments No. 8 and 9, yellowish-green deposits accumulated on the walls of the air cooled condenser, indicating that volatile chlorides were actually formed from the delayed coke. No attempt was made to analyze these deposits. When the product coke from these

two experiments is burned the resulting ash is a dark brown in colour, while the ash from product coke from all other experiments is a very light brown.

The extent of mineral matter removal from the delayed coke, under the experimental conditions employed, would seem to suggest that the inorganic constituents in the delayed coke are tightly bound within the coke structure with limited access to them by chlorine. As a comparison, Imperial and Walker (11) obtained mineral matter removals of 3% and 83% for chlorination of anthracite for 1 hour at temperatures of 600°C and 1400°C, respectively. The high chlorine and volatile contents of the coke products obtained from the high temperature chlorination experiments indicate that chlorine readily diffuses into the coke structure. but the product chlorides, having a larger molecular or collision diameter, probably cannot diffuse out. Note that the anthracite coal used by Imperial and Walker had a micropore surface of 247 m^2/g compared with the figure we determined of 117 m^2/g for the delayed coke.

4.3 High Temperature Chlorination of Ammonia Treated Delayed Coke

This final experiment, with ammonia treated delayed coke, was conducted using nitrogen and chlorine as the fluidizing gas to the electrothermal fluidized-bed reactor. Reaction conditions are given in Table 10 along with the results obtained.

When compared with original delayed coke, the ammonia treated coke showed an increased volatile content with a correspondingly lower content of carbon. Also, the coke was still non-conductive after ammonia treatment. From mercury porosimetry data, the ammonia treated coke was determined to have a macropore volume of 0.04 cc/g with a corresponding surface area of 3.29 m^2/g. This represents a slight increase in the pore volume and surface area over that obtained for the original delayed coke as reported earlier.

The size reduction, electrical resistivity, and chlorine retention of the product coke from experiment No. 10 exhibited the same characteristics as those reported for the previous chlorination experiments. One noticeable change from the previous chlorination experiments is that the product coke volatile content is lower than the volatile content of the product from untreated delayed coke. This suggests that once the volatile chlorides are formed, they may be able to diffuse out of the coke structure. This could be due, in part, to the increased porosity produced by ammonia treatment.

On a moisture, chlorine, and volatile free weight basis, the -80+100 and -100 mesh ranges of product coke contained 23.93% and 28.57% less sulphur, respectively, than the original delayed coke. This agrees with the previous trend reported for the chlorination of original

delayed coke at temperatures above 1200°C, where the difference in sulphur content between the product coke and original delayed coke remained essentially constant at about 27%.

On a moisture, chlorine, and volatile free weight basis, the -80+100 and -100 mesh ranges of product coke contained 43.40% and 22.96% less mineral matter, respectively, than the original delayed coke. This is quite an increase in mineral matter removal when compared with the chlorination of untreated delayed coke at a comparable reaction temperature and time. Once again, the slight increase in pore volume due to ammonia treatment could be responsible for this increase in mineral matter removal.

As experienced in the previous chlorination experiments above 1200°C, yellowish-green deposits accumulated on the walls of the air cooled condenser, suggesting that volatile chlorides were actually formed. These deposits were not analyzed. The ash from the product coke in this experiment was also a dark brown colour.

Table 10

Results of High Temperature Chlorination of Ammonia Treated Delayed Coke

Experimental No.		Original Delayed Coke	Ammonia Treated Delayed Coke	10	
Reaction Temp. (°C)		--	--	1511±64	
Reaction Time (MIN)		--	--	13	
Molar Percentage Cl_2 in Fluidizing Gas		--	--	3.45	
Inlet Temp. of Fluidizing Gas (°C)		--	--	175	
Weight % of Product Coke Less Than 100 Mesh		--	--	67.45	
Coke Mesh Range		-80+100	-80+100	-80+100	-100
Electrical Resistivity (OHM-CM)		∞	∞	$7.0_2 \times 10^2$	$1.3_2 \times 10^2$
Weight % Moisture		0.56	0.85	0.74	1.04
Weight % on a dry basis	Total Carbon	83.35	78.77	91.66	91.38
	Total Sulphur	5.12	5.32	4.16	3.91
	Chlorine (Cl)	0.00	0.00	1.87	2.32.
	Ash	2.90	2.50	1.76	2.39
	Volatiles (by difference)	8.63	13.41	0.54	0.00
	TOTAL	100.00	100.00	100.00	100.00

4.4 Summary and Comparison of Experimental Results

4.4.1 Resistivity

At the higher temperature used in this experimental study, the pyrolyzed coke exhibited a higher resistivity than the chlorinated coke and the chlorinated ammonia treated coke exhibited about the same resistivity as the chlorinated untreated coke. This observed increase in conductivity due to chlorination suggests that the retention of chlorine on the coke may be contributing to the conductivity, once a sample is treated above ~800°C. These results possibly suggest that the resistivity is controlled primarily by contact resistance between particles and not the resistance within the particles. These findings are supported by the work of Imperial and Walker (11) in anthracite.

4.4.2 Chlorine Retention

A problem in any eventual commercial exploitation of chlorination treatment is the ability of the delayed coke to retain chlorine after high temperature exposure. Apparently chlorine chemisorbs at high temperatures, probably on peripheral carbon atoms and probably via an ionic bond. Not only does the anthracite data support this view, the correlation of chlorine retention with the resistivity of the chlorinated coke provides further key evidence. Since chlorine is a strong electron acceptor, the retained chlorine depopulates electrons from the carbon atom on which chlorine is chemisorbed increasing the "hole" concentration and thereby the electrical conduction of the carbon.

It was found that substantial portion of the chemisorbed chlorine could be desorbed by fluidization at 1000°C with nitrogen, (experiment No. 6).

4.4.3 Ash and Sulphur Removal

To be able to compare the results from all the experiments, Figures 11,12 and 13 were constructed with the percentage difference in sulphur, ash, and carbon contents, respectively, between the product coke and the original delayed coke plotted against the average reaction temperature. The percentage increase or decrease in each constituent was calculated on a moisture, chlorine, and volatile free weight basis. The three graphs are related in the sense that a decrease in the content of one constituent may appear either as an increase in the contents of the other two constituents, or as an increase in the content of only one of the two if the content of the other one is also decreasing. The curves on each graph represent the results for chlorination times of 10 to 15 minutes.

The sulphur content of the product coke steadily decreases with increasing reaction temperature (Figure 11), until a maximum decrease of 30% is reached at approximately 1175°C. At this temperature the removal of sulphur declines as the removal of mineral matter is initiated. At about 1350°C, the removal of sulphur reaches a limit of 27%. Figure 12 shows that the removal of mineral matter continues to increase with reaction temperatures in excess of 1150°C. Therefore, at a chlorination temperature of 1500°C for a reaction time of 10-15 minutes, the product coke contained 27.0% less sulphur and 14.5% less ash. These results are reflected in the curve for the increase in carbon content of the product coke (Figure 13). The first increase in carbon content resulted from the removal of sulphur and the second increase resulted from the removal of mineral matter.

Examination of Figure 11 shows that high temperature pyrolysis at 1490°C for 5 minutes (experiment No. 1) produced a coke product with essentially the same sulphur content as produced by high temperature chlorination for 10 minutes. Remembering that experiment No. 4 and 5 were conducted using different molar percentages of chlorine in the fluidizing gas with comparable chlorination temperatures and times, the figure indicates that the removal of sulphur was independent of chlorine concentration in the fluidizing gas. Experiment No. 9 was conducted for a chlorination time of 60 minutes. Longer contact time increased the amount of sulphur removed. Ammonia treatment of the delayed coke before chlorination (experiment No. 10) did not apparently improve the removal of sulphur above that obtained for chlorination of original delayed coke under comparable experimental conditions; however, the much higher removal of ash experienced in Exp'N. 10 distorts the effective difference to some degree.

These results lead to the conclusion that the removal of sulphur was independent of chlorine concentration and depended solely on the reaction temperature and time. This conclusion is supported by the work of Imperial and Walker (11), who reported that sulphur reduction from anthracite was primarily a function of the heat treatment temperature and not of the treating atmosphere. The results also suggest that the sulphur content of the delayed coke was primarily in the condensed ring structure of the delayed coke. Thus, sulphur removal depends on the organic composition of the coke and perhaps on diffusion.

Examination of Figure 12 shows that high temperature pyrolysis at 1490°C for 5 minutes (experiment No. 1) had no effect on the removal of mineral matter from the delayed coke.

Figure 11.
Difference in Sulphur Content Between Product Coke and Original Delayed Coke vs. Average Reaction Temperature

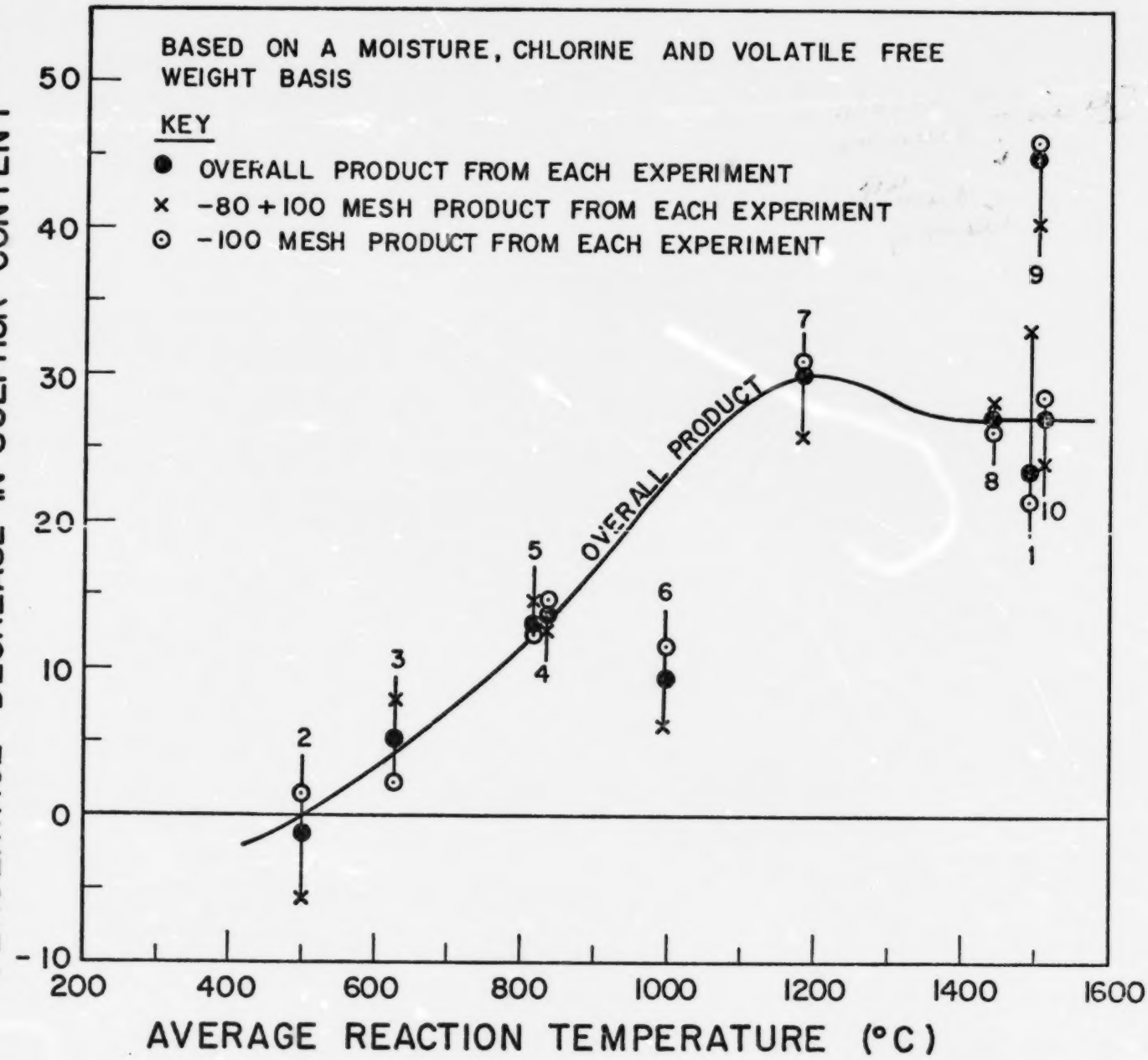


Figure 12

DIFFERENCE IN ASH CONTENT BETWEEN PRODUCT COKE AND

ORIGINAL DELAYED COKE VS. AVERAGE REACTION TEMPERATURE

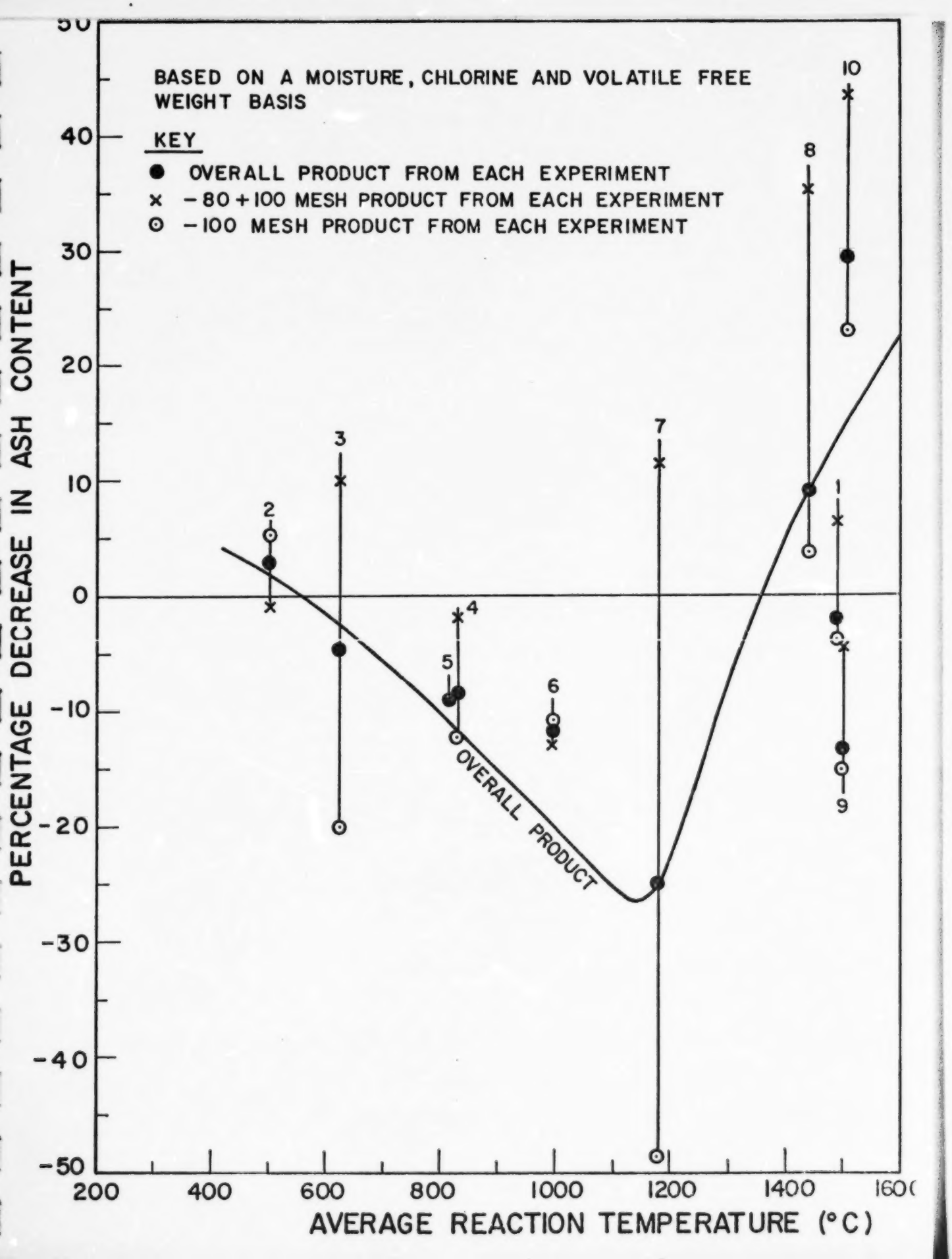
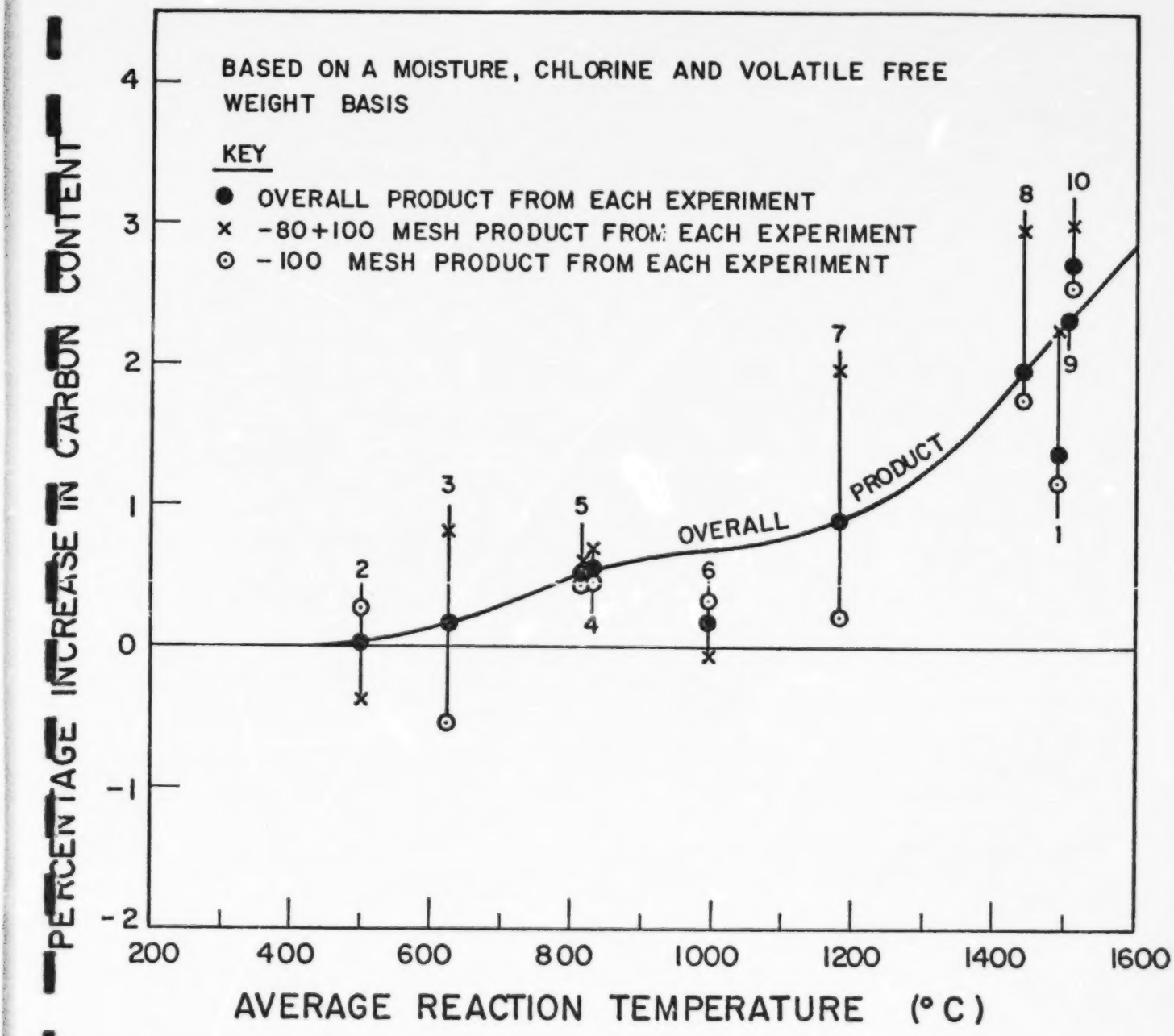

BASED ON A MOISTURE, CHLORINE AND VOLATILE FREE WEIGHT BASIS
KEY
● OVERALL PRODUCT FROM EACH EXPERIMENT
× −80+100 MESH PRODUCT FROM EACH EXPERIMENT
⊙ −100 MESH PRODUCT FROM EACH EXPERIMENT
PERCENTAGE DECREASE IN ASH CONTENT
AVERAGE REACTION TEMPERATURE (°C)
OVERALL PRODUCT
50
40
30
20
10
0
-10
-20
-30
-40
-50
200
400
600
800
1000
1200
1400
1600
1
2
3
4
5
6
7
8
9
10

Figure 13.
Difference in Carbon Content Between Product Coke and Original Delayed Coke vs Average Reaction Temperature



Experiment No. 6 was run for 10 minutes with a relatively high molar percent of chlorine in the fluidizing gas and a temperature close to 800°C. At that point, chlorine was eliminated from the fluidizing gas and the temperature in the reactor quickly raised to about 1000°C and held for another ten minute period. Depending on the size fraction, approximately 75 to 90% of the chemisorbed chlorine was removed by this treatment. However, this was the only apparent effect of the 200°C temperature rise.

Extension of the time of chlorination to 60 minutes (experiment No. 9) did not increase mineral matter removal. However, ammonia treatment of the delayed coke before chlorination (experiment No. 10) improved the removal of ash above that obtained for chlorination of the orginal delayed coke, under comparable experimental conditions. A wide spread in ash content between the -80+100 mesh and -100 mesh product coke was found, as shown in Figure 12. The removal of mineral matter from the smaller particles tended to be more difficult; no logical reasons for this observation can be developed.

These results lead to the conclusions that the removal of mineral matter depends on the presence of chlorine. The removal of mineral matter from the delayed coke may be limited by the location of the mineral matter within the coke structure. It may well be completely inaccessible to chlorine due to closed or very fine pores. Thus, even if chlorine could diffuse in, the product chlorides, having a larger collision diameters, could not diffuse out. If the delayed coke possessed a structure like that of anthracite, almost complete removal of mineral matter by chlorination at 1500°C for 10 minutes should have resulted, as reported by Imperial and Walker (11).

4.4.4 Scanning Electron Microscope Studies

In the hope of achieving a better understanding of the structure of the delayed coke, a number of original delayed coke, ammonia treated coke, and product coke samples were examined using a scanning electron microscope (SEM).

Some representative micrographs from this study are presented in Figures 14-22. The effect of ammonia treatment on the delayed coke can be seen by comparing Figure 15 with Figures 17 and 18. Ammonia treatment appears to cause the formation of numerous minute fractures in the delayed coke. This could explain the observation that the pore volume measured by mercury porosimetry increased slightly after ammonia treatment.

Appearance of the coke surface after heating to 1500° in the presence of N_2 (experiment No. 1) can be seen in Figure 19. Pitting of the surface and debris evident in the micrograph suggest either surface devolatilization or possibly the effects of abrasion in the fluidized bed. It is not known whether this is an isolated phenomena or whether it is typical of the surfaces of all the particles.

Much less debris appears in Figures 20 and 21 which show the surface after high temperature chlorination. Figure 21a shows a severely fissured, smooth area. This area shows a remarkable resemblance to carbonized liquid crystals (carbonaceous mesophase) formed from petroleum pitches pyrolyzed at $\geq$ 500°C described by Zimmer and White[30]. Pysz and Heinz[31] attribute the fissure to shrinkage on cooling of the mesophase. It is unlikely that the surface is related to chlorination.

Figure 22 shows the micrographs of coke pretreated with ammonia and then chlorinated at 1510°C. Difference in the samples shown in Figure 12 are minor despite the wholly different face of the particle seen in the micrograph. There appears to be somewhat more debris and the fissures are considerably larger.

A number of the micrographs (Figures 16b, 17a, b) shows nodules on the surfaces. These hemispheres have diameters ranging from 2 to about 15 microns. It is likely that these nodules are regions of solidified, partially carbonized mesophase. An extensive literature on the coking of coal and petroleum pitches exists[32]. Bitumen is largely pitch so it should behave similarly to petroleum pitch. It is known that pitch depolymerizes or cracks as it is heated above 300°C. Repolymerization occurs to form flat, poly nuclear structures of low H/C ratios as typified by decacyclene. These disc like molecules are capable of long range orientation to give liquid phase crystals known as mesophase. The size of these liquid crystals is measured in microns and they are spherical in shape. When temperatures reach above 400°C, the liquid phase solidifies and the solidified mesophase is highly anisotropic providing a readily visible region under an optical microscope with polarized light. In regions of the repolymerizing pitch where long range orientation is obstructed, some orientation occurs, but the tiny crystallites are formed with random inclination to one another so that the coke in these regions is isotropic. The solidified mesophase is the precursor of graphite which begins to form above 600°C.

Parkash and Berkowitz have recently reported[33] on the

mesophase behaviour of pitch derived from tar sands. They detected spherical mesophase bodies in the coke formed from tar sands pitch. Sizes are not given, but these authors report the spheroids can collect if the pitch is heat soaked for long times (as in delayed coke) to form regions which resemble what is seen in Figure 16b. Film sequences[34] of mesophase formation from petroleum pitches shows spheroids up to 35 microns can be reached after 1 1/2 hours soaking between 420 and 440°C.

Of significance for this study is that the nodules observed in some micrographs are regions of high purity carbon with probably low levels of sulfur and ash. Density of the solidified mesophase is greater than that of the remaining coke so that this may offer a route to environmentally satisfactory combustion coke.

Figure 14

S.E.M. PICTURES OF ORIGINAL DELAYED COKE

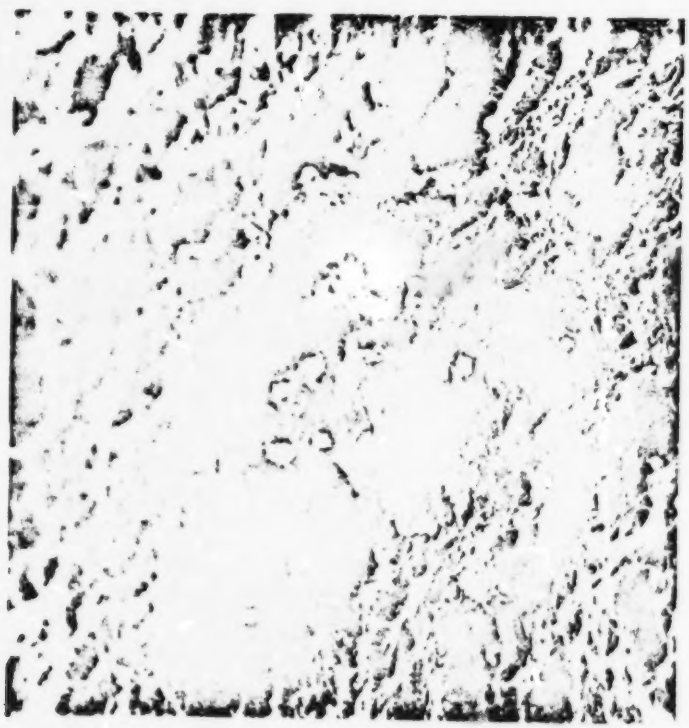


Figure 15

S.E.M. PICTURES OF ORIGINAL DELAYED COKE

6,720X

1.49 μm

(5) ORIGINAL GCOS DELAYED COKE

920X

10.97 μm

Figure 16

S.E.M. PICTURES OF NH_3 TREATED DELAYED COKE

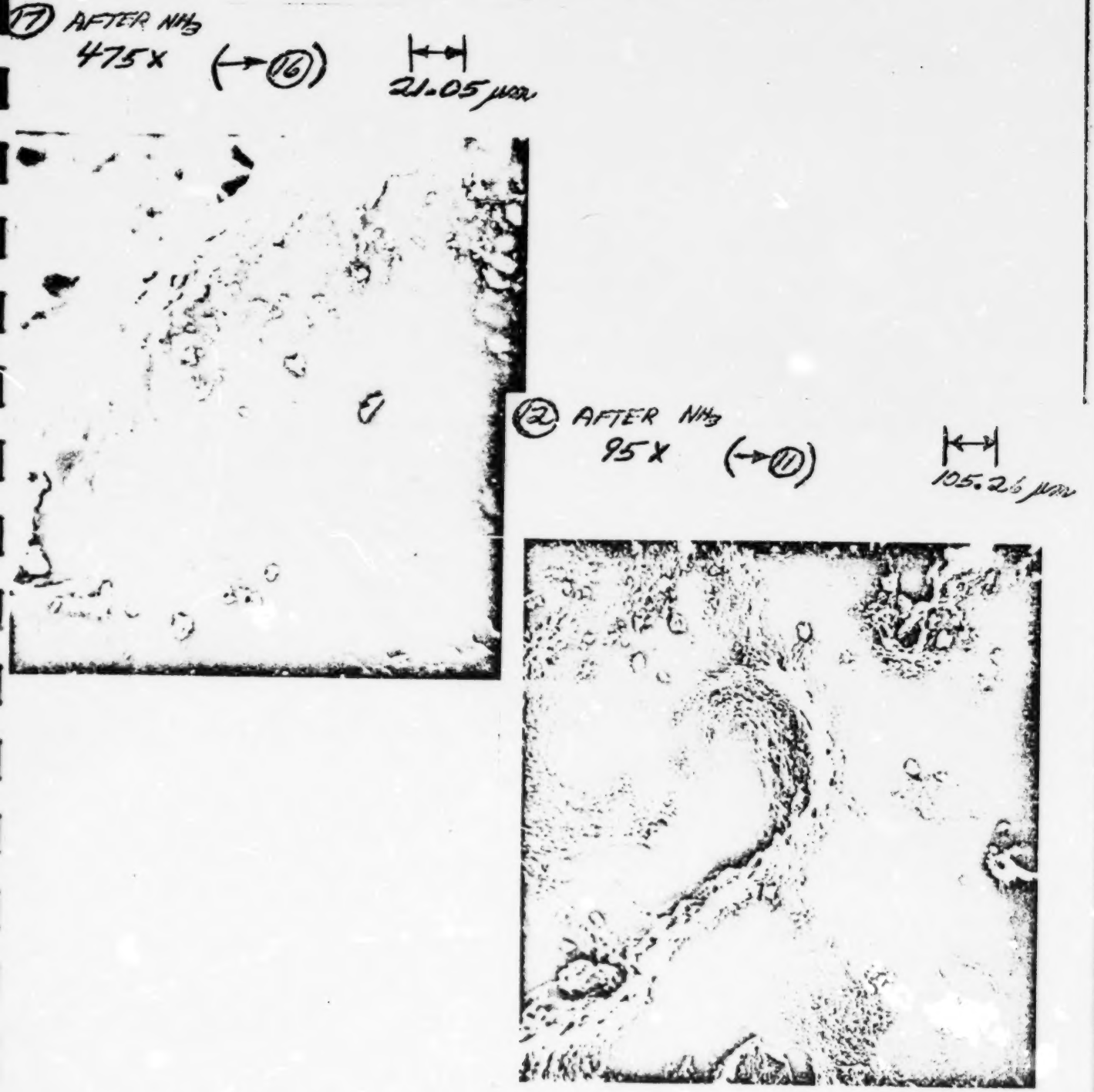


Figure 17

S.E.M. PICTURES OF NH_3 TREATED DELAYED COKE

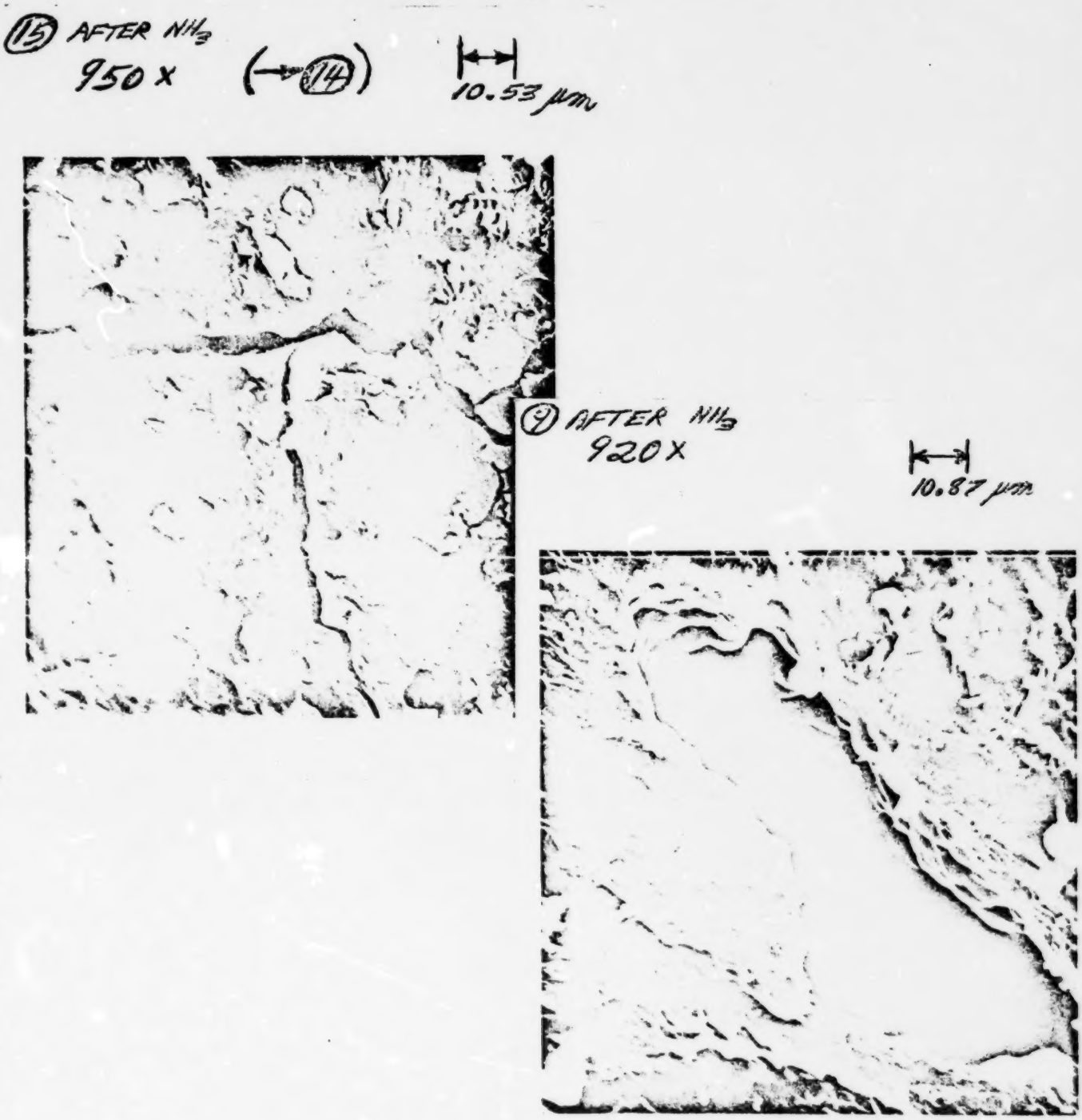
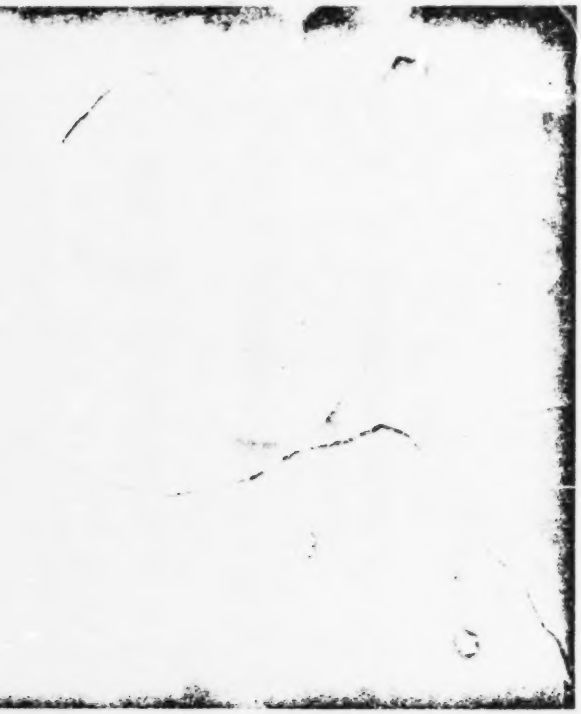


Figure 18

S.E.M. PICTURES OF NH_3 TREATED DELAYED COKE

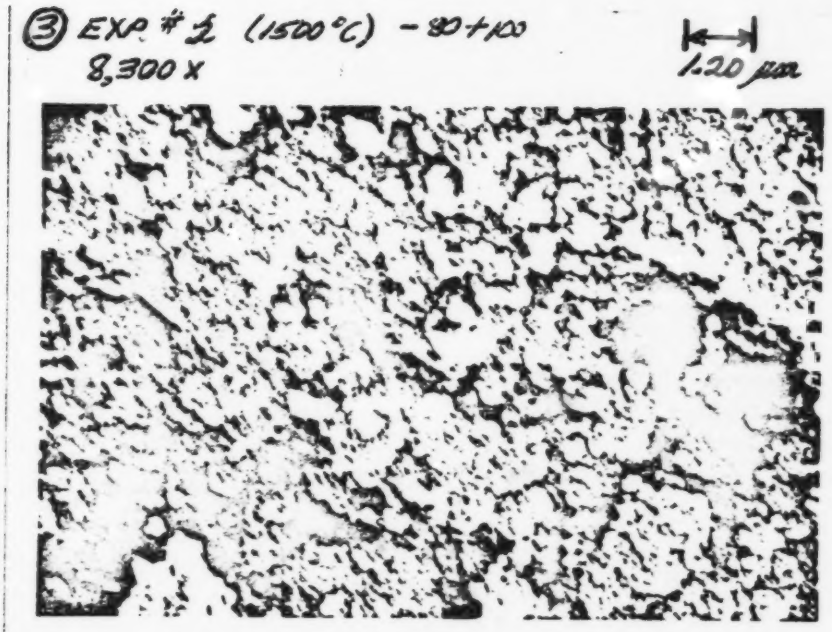
AFTER NH_3
1900 x (→ 17)
5.26 μm



(18) AFTER NH_3
950 x (→ 16)
10.53 μm

Figure 19

S.E.M. PICTURES OF PRODUCT COKE FROM EXPERIMENT No. 1



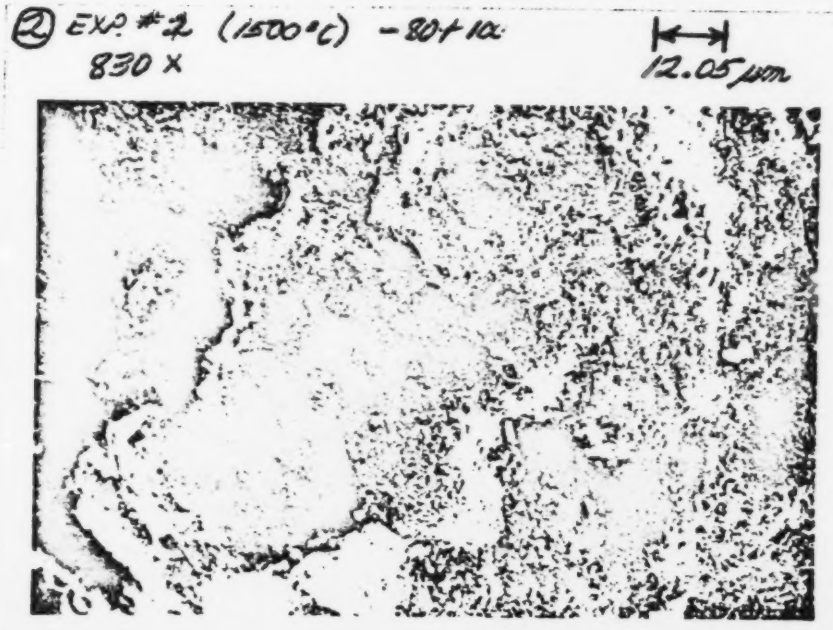
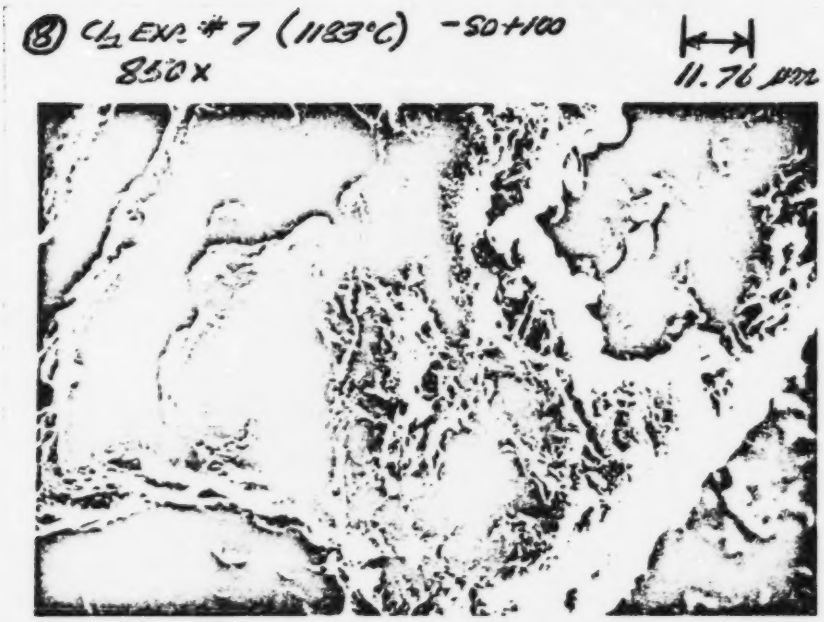


Figure 20

S.E.M. PICTURES OF PRODUCT COKE



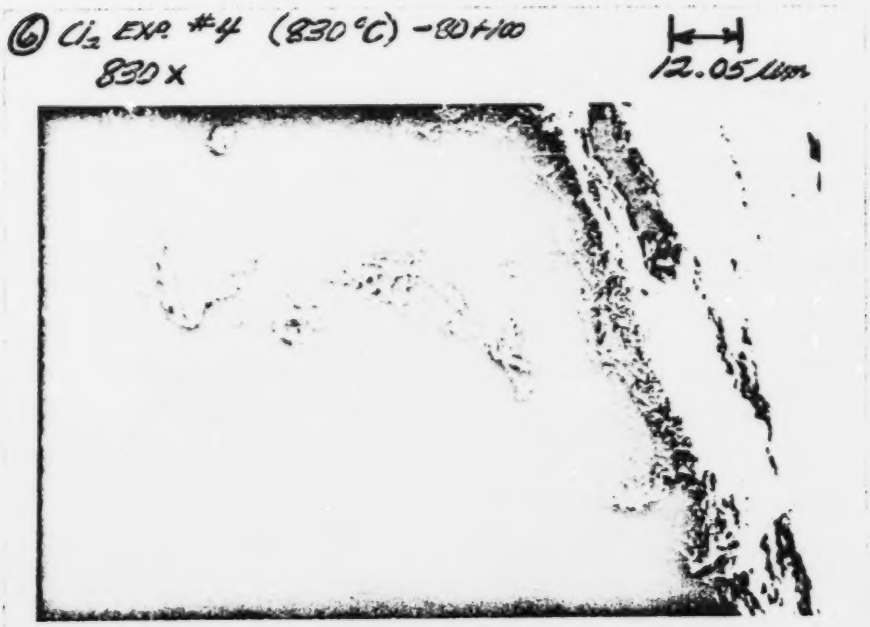


Figure 21

S.E.M. PICTURES OF PRODUCT COKE

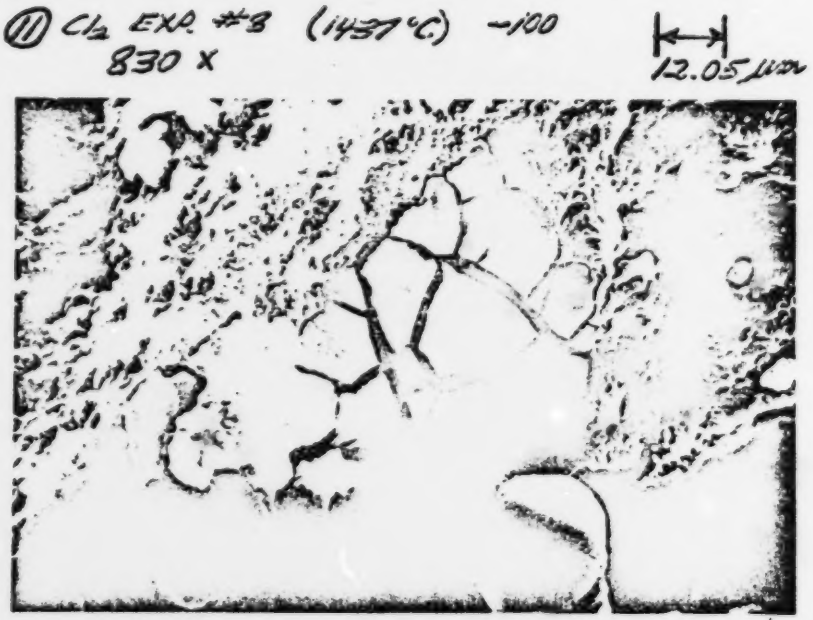
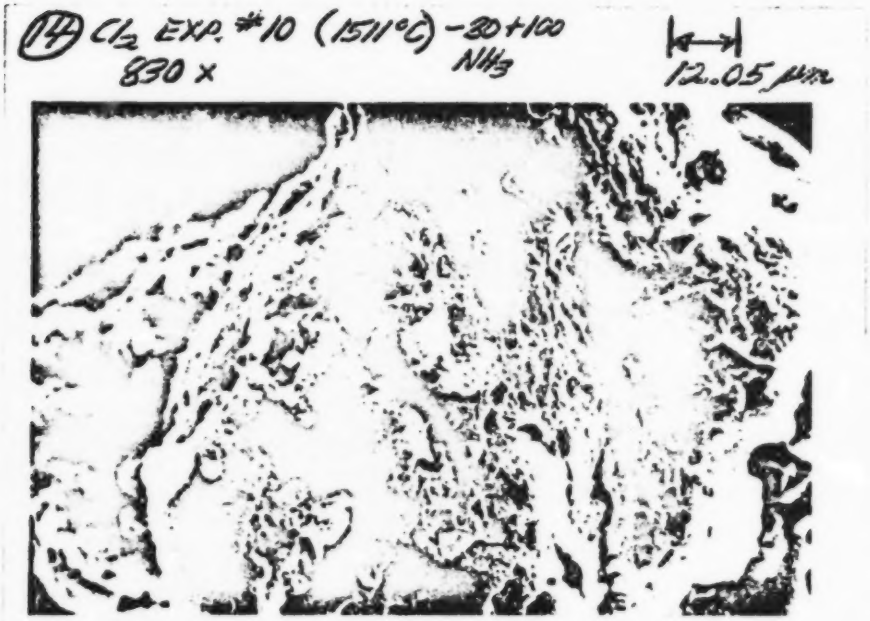
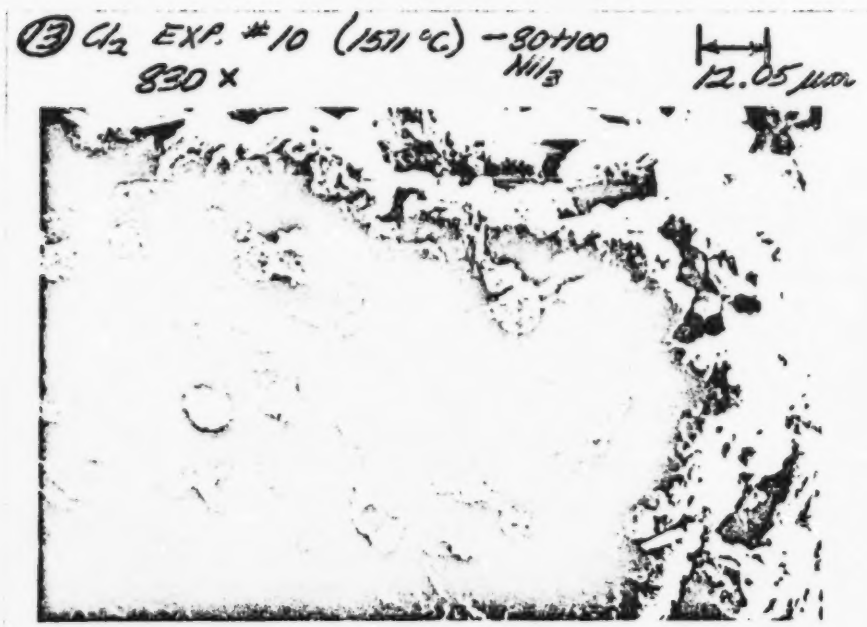


Figure 22

S.E.M. PICTURES OF PRODUCT COKE FROM EXPERIMENT No. 10





V. CONCLUSIONS

1. Pyrolysis of delayed coke, up to a reaction temperature of 1500°C in an electrothermal fluidized-bed reactor, was partially effective in the removal of sulphur, but was not effective in the removal of mineral matter. High temperature pyrolysis of original delayed coke, at 1490°C for 5 minutes, produced a coke product with 23.55% less sulphur, on a moisture, chlorine, and volatile free weight basis. We believe that the sulfur removal is primarily by the thermal cracking of refractory thiophenes and their derivatives.

2. Chlorination of delayed coke at temperatures between 800 and 1500°C in a fluidized bed reduces the sulfur content of the coke by up to about 27% and the ash content by up to about 10%, depending upon the time of contact, Cl_2 partial pressure and the temperature (all figures on a moisture, chlorine and volatile free weight basis). It is believed that ash removal is limited by diffusivity of the chlorinated products which is low because of the low fine porosity of the coke even after heating.

3. Pretreatment of coke with NH_3 at 750-800 kPa and 21°C followed by high temperature chlorination in a fluidized bed gives sulfur removal to ca. 27% and substantially raises ash removal to ca. 30%. Apparently, NH_3 pretreatment increases the porosity of the coke and increases the diffusivity of the chlorination products out of the coke structure.

4. Problems to be overcome in further development of a high temperature chlorination process are:

a) the retention of Cl_2 in the coke. Values as high as 7% Cl_2 were measured, although Cl_2 recovery was demonstrated to be enhanced by stripping the coke at elevated temperatures.

b) Delayed coke is non-conducting. Although this problem was partially solved by operating with the reactor initially loaded with coarse petroleum coke which is conductive and then blowing delayed coke powder in with the fluidizing gas, this complicates operation of the reactor and adds further sources of breakdown. A simple preheating step can be used to effect electrical conductivity of the coke.

c) Severe operating difficulties, even on a bench scale, were experienced by the combination of high temperatures, chlorine and the delayed coke powder. Solving these problems will call for a substantial research effort.

5. Photomicrographs made by S.E.M. disclosed planes of spheroids ranging from 2 to 15 microns in diameter in the heat treated delayed coke. These appear to be solidified mesophase. As mesophase is usually more dense than isotropic carbon and is very low in sulfur and ash, our observations suggest sulfur removal and metals recovery from the ash could be affected by fine grinding of the delayed coke followed by dense media separation. The delayed coke is very friable so fine grinding would not pose a problem.

Along with specific process conclusions, we find generally that the results are encouraging for a preliminary investigation even though the sulfur and ash removals achieved are well below the removal levels achieved by the chlorination of anthracite. Sulfur and ash removals are large and chlorinations may be attractive as an alternative to stack gas scrubbing. The research has opened many promising avenues to pursue and has identified process problems which must be solved.

6. The electrothermal fluidized bed reactor, while an interesting concept in heating as it separates the reactions from the method of heating, may not be the best method of heating for this type of experimental work. The use

of oxygen to provide combustion heat may open up the pore structure of the coke to provide improved paths for diffusion of chlorine into the coke and chlorinated products out of the coke.

7. To provide higher temperatures with the electrothermal fluid bed reactor for the treatment of delayed coke, a larger power source would be required. This is because, for some reasons not completely understood, the bed mixture we used tended to defluidize very easily, thus requiring higher gas flows than normally used. The higher gas flows expanded the bed and introduced a very high bed resistance that was difficult to handle with the existing power source.

VI. RECOMMENDATIONS

1. Results obtained fulfill the data requirements for an economic assessment of high temperature fluidized bed chlorination. Such an economic study should be undertaken to see whether the process is competitive with stack gas scrubbing or alternatives such as fluid bed combustion with dolomite injection. An economic study will indicate cost sources and assist in directing the goals of future research.

2. Coke after chlorination should be tested to see if the treatment improves the combustibility of coke.

3. Ammonia pretreatment followed by chlorination should be studied in much more detail. Influence of particle size, NH_3 pressure, contact time, chlorine particle pressure and temperature on sulfur and ash removal should be investigated.

4. Reactors other than a fluidized bed should be considered.

5. Separation of solidified mesophase from isotropic carbon, probably by dense media should be explored.

VII. REFERENCES CITED

1. Walker, L.A., Luhning, R.W., and Rashid, K., Potential for Recovering Vanadium from Athabasca Tar Sands, Paper presented at the 26th Canadian Chemical Engineering Conference, Toronto, Ontario, October 3-6, 1976. Toronto, Ontario: CSChE, 1976.

2. Humphreys, R.D., "Some Engineering Aspects of the G.C.O.S. Tar Sands Project". CIM Bulletin, December, 1974, pp. 67-70.

3. Webster, I.C., Personal letter, Acting Chief Process Eng. at G.C.O.S., Edmonton, Alberta, October 30, 1978.

4. Egglestone, A.E. and Wise, T.H., Athabasca Oil Sands-Developments in Extraction and Upgrading. Paper presented at the 26th Canadian Chemical Engineering Conference, Toronto, Ontario, October 5, 1976. Toronto, Ontario: CSChE, 1976.

5. Sermon, G.T., Report No. AECD-3912, U.S. Atomic Energy Comm., 1948.

6. Sermon, G.T., and Brooks, L., Report No. AECD-3913, U.S. Atomic Energy Comm., 1949.

7. Juel, L.H., Report No. AECD-2758, U.S. Atomic Energy Comm., 1952.

8. Aluminum Laboratories Ltd., Montreal, Canada, Brit. 716,718, October 13, 1954.

9. Hartwick, E.F., Miners, K.A., and Phillips, N.W.F., to Aluminum Laboratories Ltd., Canada, U.S. 2,698,777, January 4, 1955.

10. Odening, C.A. and Bowman, J.C., Industrial Carbon and Graphite. London: The Society of Chemical Industry, 1958, p. 537.

11. Imperial, G.R. and Walker, P.L., Jr., Mineral Matter Removal from Anthracite by High Temperature Chlorination. Special Research Report, No. SR-31, Submitted to the Coal Research Board of the Commonwealth of Pennsylvania. University Park, Pennsylvania: The Pennsylvania State University, March 26, 1962.

12. Starzonski, J.J., and Brothers, J.A., Desulphurization: Research and Development at Nova Scotia Research Foundation Corporation. Paper presented at the 28th Canadian Chemical Engineering Conference, Halifax, Nova Scotia, October 22-25, 1978. Ottawa, Ontario: CSChE, 1978.

13. Kellogg, H.H., "Thermodynamic Relationships in Chlorine Metallurgy". Journal of Metals, Vol. 188 (June, 1950), pp. 862-872.

14. Almagro, G. and Walker, P.L., Jr. Chlorination and Activation of Pennsylvania Anthracites. Special Research Report, No. SR-59, submitted to the Coal Research Board of the Commonwealth of Pennsylvania. University Park, Pennsylvania: The Pennsylvania State University, October 24, 1966.

15. Leco Corporation, Titrators Instruction Manual. St. Joseph, Michigan: Leco Corporation, 1975.

16. Leco Corporation, Gasometric Carbon Analyzer Instruction Manual, St. Joseph, Michigan: Leco Corporation, 1974.

17. American Society for Testing and Materials. Gaseous Fuels: Coal and Coke, 1973 Annual Book of ASTM Standards, Part 19. Philadelphia, Pa.: American Society for Testing and Materials, 1973.

18. Pradhan, Dr. N.K., Coal and Petroleum Analysis by Atomic Absorption Spectroscopy. Springvale, Australia: Varian Techtron Pty. Ltd., March, 1976.

19. Aminco, Aminco Digital Readout Porosimeter. Silver Spring, Ml.: American Instrument Co., Inc., January, 1967.

20. Orr, C., Jr., and Dallavalue, J.M., Fine Particle Measurement. New York: Macmillan Co., 1959.

21. Cranston, R.W. and Inkley, F.A., "The Determination of Pore Structures from Nitrogen Adsorption Isotherms". Advances in Catalysis, Vol. 9, (1957), pp. 143-154.

22. Ponec, Dr. V., Knor, Dr. Z. and Yerny, Dr. S., "Theory of Adsorption Equilibria". Adsorption on Solids. Edited by D. Smith and N.G. Adams. Czechoslovakia: Butterworths and Co. Ltd., 1974.

23. R-I Controls Division, Instruction Manual Phaser Solid State Power Controller. Minneapolis, Minnesota: R-I Research Inc., 1971.

24. R-I Controls Division, Instruction Manual Thermac Series 6000 Temperature Controller. Minneapolis, Minnesota: R-I Research Inc., August, 1971.

25. Syracuse Research Corp., Clean Coal-Improving the Product by Chemical Comminution. Syracuse, New York: Syracuse Research Corp., December 1976.

26. Keller, D.V., Jr., and Smith, C.D., "Spontaneous Fracture of Coal", Fuel, Vol. 55 (October, 1976), pp. 273-280.

27. Cullen, P.D., and Quackenbush, V.C., Chemical Comminution - An Improved Route to Clean Coal. Paper presented at the 28th Canadian Chemical Engineering Conference, Halifax, Nova Scotia, October 22-25, 1978. Ottawa, Ontario: CSChE, 1978.

28. Aldrich, R.G., "Spontaneous Fracture of Coal", Letter to the Editor, Mohawk Power Corp., Syracuse, New York, February 7, 1977. Fuel, Vol. 56 (July, 1977), p. 345.

29. Howard, P.H., Datta, R.S., and Hanchett, A., "Chemical Fracture of Coal for Sulphur Liberation". Letter to the Editor, Syracuse Research Corp., Syracuse, New York, March 7, 1977. Fuel, Vol 56 (July 1977), p. 346.

References

30. J.E. Zimmer and J.L. White, "Core Structure of Disclinations", p. 429, Extended Abstracts, 14th Biennial Conf. on Carbon, June, 1979, Penn State.

31. R.W. Pysz and E.A. Heintz, "Mesophase Development on a Carbon Substrate", p. 427, Extended Abstracts, 14th Biennial Conf. on Carbon, June, 1979, Penn State.

32. J.L. White, "Petroleum Derived Carbons", A.C.S. Symp. Series 21, 315. Am. Chem. Soc. (Washington, 1976); T.D. Brooks and G.H. Taylor, Carbon 3, 185 (1965), J.L. White, Prog. Solid State Chem. 9, 59 (1975).

33. S. Parkash and N. Berkowitz, "Mesophase Behaviour of Bitumen Pitch from Oil Sands in Early Stages of Carbonization", p. 425. Extended Abstracts, 14th Biennial Conf. on Carbon, June, 1979, Penn State.

34. D.S. Hoover, A. Davis, A.J. Perrotta, W. Spackman, "Use of Cinematography in a Study of Mesophase Formation", p. 393. Extended Abstracts loc. cit.